PB86-167756

Local Source Impact on Wet Deposition

Brookhaven National Lab., Upton, NY

Prepared for

Environmental Protection Agency
Research Triangle Park, NC

Mar 86

U.S. Department of Commerce
National Technical Information Service
NTIS

TECHNICAL REPORT DATA *(Please read Instructions on the reverse before completing)*		
1. REPORT NO. EPA/600/3-86/014	2.	3. RECIPIENT'S ACCESSION NO. PB86 167567AS
4. TITLE AND SUBTITLE LOCAL SOURCE IMPACT ON WET DEPOSITION		5. REPORT DATE March 1986 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Aristides A.N. Patrinos		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Atmospheric Sciences Division Brookhaven National Laboratory Upton, Long Island, NY 11973		10. PROGRAM ELEMENT NO. CCVN1A/05 -3104 (FY-85) 11. CONTRACT/GRANT NO. DW89006701
12. SPONSORING AGENCY NAME AND ADDRESS Atmospheric Sciences Research Laboratory - RTP, NC Office of Research and Development U.S. Environmental protection Agency Research Triangle Park, NC 27711		13. TYPE OF REPORT AND PERIOD COVERED 14. SPONSORING AGENCY CODE EPA/600/09
15. SUPPLEMENTARY NOTES		

16. ABSTRACT

Precipitation chemistry measurements over a network of samplers upwind and downwind of Philadelphia, PA show that a major contribution of the local sources can be discerned under certain conditions. For winter frontal storms with low level winds from the south east, up to as much as a factor of two increase over upwind values has been observed for downwind nitrate deposition. Sulfate deposition shows an increase of about a factor of one and one half. The nitrate deposition increases toward the downwind direction away from the urban-industrial sources, indicating that the maximum is likely to have been beyond the sampling network for these case studies. One storm had no increase in nitrate or sulfate deposition but did have an increase in total sulfur content in the precipitation. Reasons for this difference are being sought.

17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	19. SECURITY CLASS *(This Report)* Unclassified 20. SECURITY CLASS *(This page)* Unclassified	21. NO. OF PAGES 77 22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

PB86-167756

EPA/600/3-86/014
March 1986

LOCAL SOURCE IMPACT ON WET DEPOSITION

by

Aristides A. N. Patrinos

Brookhaven National Laboratory
Upton, Long Island, New York 11973

DW89006701

Project Officer

Francis S. Binkowski
Meteorology and Assessment Division
Atmospheric Sciences Research Laboratory
Research Triangle Park, North Carolina 27711

ATMOSPHERIC SCIENCES RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27711

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

DISCLAIMER

The information in this document has been funded wholly or in part by the United States Environmental Protection Agency under Interagency Agreement Number DW89006701 to the Brookhaven National Laboratory. It has been subject to the Agency's peer and administrative review, and it has been approved for publication as an EPA document. Mention of trade names or comercial products is does not constitute an endorsement or recommendation for use.

ABSTRACT

Precipitation chemistry measurements over a network of samplers upwind and downwind of Philadelphia, PA show that a major contribution of the local sources can be discerned under certain conditions. For winter frontal storms with low level winds from the south east, up to as much as a factor of two increase over upwind values has been observed for downwind nitrate deposition. Sulfate deposition shows an increase of about a factor of one and one half. The nitrate deposition increases toward the downwind direction away from the urban-industrial sources, indicating that the maximum is likely to have been beyond the sampling network for these case studies. One storm had no increase in nitrate or sulfate deposition but did have an increase in total sulfur content in the precipitation. Reasons for this difference are being sought.

CONTENTS

Abstract iii

Figures vi

Tables vii

1. Introduction 1

2. Point Sources 5

3. Area Sources 17

4. The Philadelphia Field Study 29

Background 29

Exploratory Phase and Quality Assurance 30

The Main Field Study and General Results 35

Diagnostic Modeling of a Philadelphia Storm 52

5. Concluding Remarks 55

6. References 60

FIGURES

Number		Page
1	Sulfur IV Deposition for December, 1983 Storm	31
2	Sulfate Deposition for December, 1983 Storm	42
3	Nitrate Deposition for November, 1983 Storm	49
4	Nitrate (left) and Ammonium (Right) Deposition for April, 1984 Storm	50

TABLES

Number		Page
1	Field Studies Around Point Sources	8
2	Summary of Meteorological Characteristics of Storms	32
3	Statistical Summary of Deposition Data	38
4	Dissolved SO_2 Deposition Data for Sampled Storms	43
5	Estimates of SO_x and NO_x Emission Rates along the Deleware Valley	46
6	Diagnostic Modeling Parameters and Inputs for Storm 0405 Simulation	54

SECTION 1

INTRODUCTION

It has become increasingly apparent that the impact of local sources on acid wet deposition is of considerable importance in developing source receptor relationships and establishing fair and effective mitigation strategies; these strategies may seek the apportionment of fractions of sensitive receptor depositions to various source regions. It should be emphasized that the "local source" issue has been somewhat controversial with several studies alternatively overemphasizing or underestimating the local source contribution. Earlier studies generally tended to disregard local source contributions for several reasons. Public awareness of the "acid rain" problem was associated with discovery of alleged ecological damage (Likens et al., 1979) of remote and assumed pristine areas such as the Adirondacks in New York, the White Moutains in New Hampshire, and in several regions of Scandinavia. Claims of the rise in the acidity of some lakes resulting in fish population decreases and reports of possible forest deterioration (Johnson and Siccama, 1983) due to soil acidification have been linked to the deposition of sulfate which originated as sulfur dioxide (SO_2) at considerable distances upwind. For the Northeast, the candidate sources are the large power generating facilities of the Ohio Valley. These "tall stack" point sources provide the framework for the "long range transport" hypothesis since sulfur emissions at higher elevations would be transported by the prevailing winds and with longer atmospheric residence times would interact with available oxidants producing the sulfates which would ultimately be scavenged at the sensi-

tive receptor regions. The contribution of nitrates to the overall acidity in the above context has been considered secondary. The "long range transport" scenario was further bolstered by the evidence from field studies of wet deposition around large point sources. As will be presented in later sections, most of these studies point to a relatively small contribution from the overall emissions to the wet deposition in the near field. The equivalent results from large area sources, however, are somewhat at odds with the point source studies. These results, particularly from the recent Philadelphia field studies, have shown that the diffuse low level emissions associated with areal sources have some impact on the local scale and maximum impact on the mesoscale (within 100 km). This impact is mostly manifested with the deposition of nitrate which implicates the significant transportation sources present in large urban areas. The recognition that acidic deposition, in fact both wet and dry, would be significant on the mesoscale around large urban and industrial centers along with the realization that the eastern U.S. has a sizable number of such centers have revived the importance of the local source issue. Further support is prompted by the materials damage assessment; acidic deposition has been suspected to cause damage to structures, masonry, paint, and generally materials (Baer et al., 1984) which are in great abundance in and around area sources. The potential damage to historical landmarks, statues, etc., is of particular concern. Implicit support to the "local source" issue is provided by the realization that acidic materials which are deposited locally are not available for long range transport; thus an accurate accounting of near source deposition is important to the overall pollutant budget. Furthermore, studying

wet deposition in the near field of a large pollution source presents a convenient experimental framework with a potentially better opportunity to comprehend some of the fundamental atmospheric processes involved in acidic wet deposition, such as scavenging mechanisms and chemical reactions; this would improve the understanding of source-receptor relationships at longer scales. Having established the importance of the "local source" contribution it should be pointed out that the uncertainties in the extent, type, and frequency of this contribution are high. There are two important reasons for these uncertainties. The first is due to the paucity of available data on wet deposition in and around large area sources. In the U.S. only two comprehensive, large scale field campaigns were undertaken for the purpose of sampling wet deposition on an event basis, and those only for limited time periods. The METROMEX study (AMS, 1981) around the city of St. Louis concentrated on summer, convective storms. The Philadelphia studies were geared toward cyclonic and primarily nonconvective storms. Furthermore, most of the existing precipitation chemistry networks have purposely located their sites away from large local sources; this was dictated by the desired regional nature of these networks. As a result, it is felt that the integrated results based on these networks have consistently underestimated the total deposition budgets, particularly for nitrate. The absence of long-operating urban sites also make trend analyses such as at the Hubbard Brook Experimental Station (Munn et al., 1982) impossible. The second cause of "uncertainty" pertains to the nature of emissions. For urban and industrial centers the pollutant precursor mix is characterized by considerable variability in both the type and temporal and spatial variability.

The distribution of primary pollutants (mostly sulfur dioxide, nitric oxide, hycrocarbons) may vary considerably from city to city depending on the level of industrial activity, transportation sources, type of residential heating and others). The primary pollutant mix may also include a certain amount of sulfate (particularly from residential oil burners) and hydrogen chloride (HCl) from the combustion of materials containing chloride impurities (Iapalucci et al., 1969; Gregory, 1976; Hlavay and Guibault, 1978). HCl is a strong acid and can significantly affect cloud and rainwater acidity near its source and is washed out rapidly when rain occurs (Patrinos et al., 1983). The distribution of primary pollutants and their temporal variability (in terms of time of day, day of the week, season of the year, etc.) affects the generation of secondary pollutants such as ozone (O_3) which is derived from photochemical reactions involving hydrocarbons and nitrogen oxides, and which in turn may play an important role in acid forming reactions (Calvert and Stockwell, 1983; Richards, 1983). Urban and industrial areas are also rich sources for catalytic substances (Penkett et al., 1979) promoting these reactions.

SECTION 2

POINT SOURCES

There exists a significant body of literature on the subject of wet deposition around large point sources. Observed concentrations of the major scavenged species vary considerably, presumably as a result of variations in meteorological and background conditions and source characteristics, but often insufficient detail is available to evaluate precise scavenging characteristics. Earlier field studies were aimed toward demonstrating the efficacy of taller stacks in lessening local impacts. In fact point sources may be defined as those sources which have elevated releases because of requirements to meet ambient air quality standards on SO_x, NO_x, and particulates. They may include power plants, smelters, pulp and paper mills, petroleum refineries, cement plants, etc. The majority of the studies generally support this claim. The most notable exception has been in the deposition of trace metals for which the particulate nature of the emissions promotes efficient wet scavenging in the near field (within 25 km of the source). For the important inorganic ions found in "acid rain," sulfates and nitrates, the wet deposition in the near field represents but a few percentage points of the total emissions during precipitation. Of the observed variabilities mentioned above perhaps the most prominent is that of the background conditions particularly for sulfur. Since most of the emitted sulfur is in the form of sulfur dioxide (SO_2) its solubility in cloud or rain drops is very much a function of pH (Hales and Sutter, 1973) and consequently the

ultimate scavenging efficiency is highly dependent on background cloud and precipitation acidity. At the same time the presence of certain oxidants (such as hydrogen peroxide) (Penkett et al., 1979) or catalytic substances may accelerate the SO_2 to sulfate process increasing the wet deposition of sulfate well beyond what is estimated on the basis of primary sulfate emissions.

Another source of variability is the nature of the precipitating system. It appears that the scavenging of sulfate and nitrate may be considerably enhanced during summer convective storms compared to winter time frontal precipitation. This may be due to longer in-cloud residence times of primary pollutants in convective situations actively promoting faster acidifying processes and reactive scavenging.

Dana and Patrinos (1983) reviewed open literature results from wet deposition studies around large point sources to, primarily, compare simply calculated scavenging parameters. Table 1 is an expanded version of their table presenting most field studies around large power plants, smelters and refining installations; these projects are compared for source characteristics, sampling network, and fractional removal. Results of measured SO_2 and H^+ concentrations generally exhibited a variability of more than two orders of magnitude. The above mentioned variability in SO_2 deposition is increased further by the lack of sufficient data at greater distances.

One of the first sulfur washout experiments was conducted at the Keystone power plant in western Pennsylvania (Hales et al., 1971) by Battelle Pacific Northwest Laboratories (BNW). The primary objective was to assess the effectiveness of precipitation washout as a scrubber of sulfur compounds from the plume; the secondary objective was to evaluate the relative importance of various atmospheric conditions on washout efficiencies. Although the high background levels of acidity and sulfur prevented accurate calculations of removal rates for the Keystone plume, it became apparent that the old irreversible gas scavenging models were not appropriate for SO_2; indeed the samples showed very little SO_2 washout compared with the sulfate aerosol washout. Another early study around the Colbert County generating station in Alabama (Hutcheson and Hall, 1974) contrasted the Keystone results. A significant amount of the sulfur wet deposition was attributed to SO_2 scavenging due to the relatively "clean" background rain.

The studies around the Centralia power plant were also conducted by BNW (Dana et al., 1975; Dana et al., 1976) in a region of low background acidity and sulfur concentrations in rain. Results confirmed that the method of calculating the washout of SO_2 from plumes, based on reversible gas absorption phenomena, is applicable to circumstances involving power plant plumes emitted from tall stacks, as well as for less complicated situations; indeed, the possibility of a "negative" washout effect was demonstrated. The Centralia results also indicated that the washout of sulfur from the plume can be 1-5 times greater than that of SO_2 on a molar basis, thus emphasizing that the important sulfur compound scavenging problem is that involving sulfate. A smaller scale study was conduct-

TABLE 1. Field Studies Around Point Sources

Site	Source	Power, MW electric	Number of stacks/ height, m	Sampling Sites, km Number / Range		Species Analyzed*	Sulfur Source,† gmoles/s	X(d_f) km	Species	d_f,¶ %
Power Plants										
Pennsylvania	Keystone	§	2/240	50	2-6	SO_2, SO_4^-, H^+, NO_3^-, NO_2^-	40-95	-	-	-
Alabama	Colbert County	1400	5/90	17	2-25	S	§	-	-	-
Washington	Centralia	700	1/143	162	0.4-11	H^+, SO_2, $SO_4^=$	9.3-12	11	SO_2 $SO_4^=$	0.23-1. 0.50-3.2
Washington	Centralia	700	1/143	40	0.4	Major ions, SO_2	9.8	-	-	-
Washington	Centralia	700	1/143	85	1.4-11	Major ions, SO_2	25-33	11	SO_2 $SO_4^=$	0.55 0.73-0.96
Georgia	Bowen	3160	2/305	31	1-14	Major ions, SO_2	90	14	SO_2 Cl	0.3-1.2 32-100
Sweden	Stengungsund	860	4/85	78	3-15	S, pH, Na^+	5-24	15	S	1-6
Sweden	Karlshamm	1000	3/140	100	3.5-60	S, pH, NH_4^+	10-40	60	S	38-97
Netherlands	Flevo	§	§	60	5-15	Major ions, SO_2, metals	§	20	S	1
New York	Oswego	1230	1/213	26	2-4	M_g, $SO_4^=$, NO_3^-	90	4	$SO_4^=$	1
Smelters & Refining										
Ontario	Sudbury		1/380	50	18-70	SO_2, S, NO_3^-, Cl^-	720	50	S	0.5-1.6
Ontario	Sudbury		1/380	25	3-50	Major ions, metals	310	50 40 40	S SO_2 $SO_4^=$	5.6 0.7 48
Ontario	Sudbury		1/380	22	12.5	Major ions, metals, SO_2	220	12.5	S	0.2
Washington	Tacoma Smelter		1/§	43	3-80	Major ions	78	60	S	8
Alberta	Sour Gas Plant		§	10	§-40	$SO_4^=$, Cl^-	12	40	S	32-46,() 2**

TABLE 1 (Continued)

* S, sulfur (total of sulfate and dissolved SO_2 measured as sulfate). Major ions include S, H^+, NO_3^-, Cl^-, NH_4^+.
† Range over experiment or average as reported.
†† Distance of evaluation of d_f, fractional removal of indicated source material during precipitation.
¶ Fractional removal of indicated source material, up to X(df).
§ Not reported.
() Summer.
** Winter.

ed by the University of Maryland (Li and Landsberg, 1975) around the Chalk Point power plant with a sampling network encircling the plant (up to 5 km) and with rainwater pH found to vary between 3.0 and 5.7. A dependence of acidic washout from the plume on wind direction was noted, but the degree of correlation was unclear.

Barrie (1980) investigated the nature and fate of emissions from an isolated power plant in a shallow river valley of the Athabasca oil sands area in western Canada. The study concentrated on "total" deposition (wet and dry) with snow chemistry surveys using acrylic plastic snow corers. The snowpack had accumulated pollutants without a melt for the 70-day period November 18, 1977, to January 26, 1978. Results are in general agreement with the wet deposition studies showing a small percentage of the sulfur and nitrogen oxides emissions depositing in the near field with an order of magnitude increase in the percentage of deposited trace metals. Due to the soluble oxides of calcium and magnesium in flyash, "total" deposition near the source was more alkaline than in outlying areas.

Holt et al. (1983) used an oxygen-18 method to distinguish the primary sulfate in the total sulfate scavenged by rain around the Tennessee Valley Authority (TVA) Widows Creek Steam Plant at Stevenson, Alabama. The network of four automatic wetfall collectors (wet-only) was operated on an event basis during the summer of 1981. Results demonstrated a 300-fold higher rain scavenging efficiency for sulfate compared with that of SO_2. Of the scavenged sulfate downwind of the plant half was attributed to primary emissions.

Patrinos et al. (1983) conducted a wetfall chemistry study around the Bowen Electric Generating Plant in northwestern Georgia. The network of automatic wetfall collectors was operated on an event basis during the winter of 1981. Sulfur, hydrogen ion, and chloride ion were found to be the predominant plume related species. Concentrations in the affected regions exceeded the background levels by up to 100% in the case of sulfur and of hydrogen ion and by up to 145% in the case of chloride ion. Again, the percentage of emitted sulfur and nitrogen products which was scavenged in the near field was small; for chloride, however, it was determined that all the emitted Cl was depleted by scavenging in the near field. Approximately 20% of the sampled storms exhibited substantial plume SO_2 scavenging.

Several major field studies around oil-fired power plants have been conducted in Europe. Granat and Rhode (1973) investigated the wet deposition around the Stenungsund plant on the western coast of Sweden, while Enger and Högström (1979) conducted a study at the Karlshamn site on the Baltic shore. The experimental plans were similar (sampling on an event basis, frontal type storms), but the results were considerably different in terms of observed deposition of plume related material and background concentrations. Results around Stenungsund indicated that the additional (above background) wet deposition of H^+ would be no greater than 10% to 15% within 15 km of the plant and the sulfur percentage would be an order of magnitude less. For the Karlshamn study the authors concluded that two thirds of the emitted material was deposited within 100-200 km from the source; for one case with high relative humidity they

reported that 70% of the sulfur from the plant occurred as sulfate and was scavenged within the first 30 km. This result appears somewhat at odds with the results from most other studies. Enger and Högström attributed the implied rapid SO_2 to $SO_4^=$ conversion to ammonia catalysis. A field study around the Flevo plant in the Netherlands (Slanina et al., 1983) employed tracer techniques to detect the plume location and measured dissolved SO_2 in the rainwater samples. The experiment found that most of the plume related sulfur wet deposition was in the form of SO_2 out to 15 km.

In the U.S., Stamm et al. (1984) sampled wet deposition downwind of an 1230 MWe oil-fired power plant in Oswego, NY, which burns high sulfur oil (ca. 2.8%); magnesium oxide is added to the effluent to protect the stack. Sampling was limited to two precipitation events on two consecutive days associated with a cyclonic weather system. For both events the plume was imbedded into a low stratus cloud. It was found that due to the MgO the acidity immediately downwind of the stack decreased compared with background and returned to background values at 4 km. Sulfate values were somewhat higher than background values but not nitrate. Vanadium (V) was used as a tracer for plume location.

The nickel smelting industries in Sudbury, Ontario, have emitted between 1.5 and 2.7 x 10^6 metric tons of SO_2 per year for a minimum of 25 years; the single 381m stack (INCO Ltd) represents the largest anthropogenic point source in the world (Summers and Whelpdale, 1976). Sudbury has been the site of a series of wet deposition field studies. Wiebe and Whelpdale (1977) examined precipitation concentration measurements of SO_2, total sulfur, and trace metals out to 70 km from the INCO stack.

They determined that less than 1% of the sulfur emitted during a precipitation event was deposited within 50 km of the source, whereas the fraction for trace metals was at least an order of magnitude higher. Slightly elevated nitrate concentrations were observed, but chloride appeared to be at background levels under the plume. A later, more extensive sampling, project examined 31 events over two years (Chan et al., 1982; Chan et al., 1984a). Samplers were of the bulk variety and were replaced on a 24h basis. For most species the wet deposition was attributed to sources other than the INCO smelter; the exceptions were Cu and Ni for which the increase, above background, was an order of magnitude. Most particulate constituents (acids, sulfates, trace metals) were scavenged quite efficiently; however, sulfur which was emitted mostly as SO_2 had low scavenging efficiency. On the average, during precipitation events, the INCO smelter was found to contribute ca. 70% of total wet deposited Cu and Ni and ca. 20% of the other trace metals and sulfur within 40 km of the stack. For events classified as cold front (west and northwest trajectories) the ratios of plume-related to background wet deposition of sulfate and nitrate were higher by a factor of two over the warm front events (south and southwest trajectories). In terms of emissions the percentage of wet deposited sulfur within 40 km was in line with most other studies (ca. 1%). The dry deposition contribution was estimated to be considerably larger.

A parallel study was undertaken during the mid-1978 to mid-1980 period in the Sudbury basin. The study was aimed toward the cumulative precipitation quality (Chan et al., 1984b) with a network of automatic

wetfall collectors (wet only); collection was undertaken on a monthly basis. During most of the first year of operation the INCO smelter was shut down. Comparisons between the data corresponding to the shutdown and the operation revealed no statistically significant differences in the acidity and the concentrations of inorganic species and most trace metals. It was argued that wet deposition was largely governed by long range transport, local wind-blown dust and vehicular traffic.

Scheider et al. (1981) compared bulk deposition data (which included both wet and dry inputs) at eight sites near Sudbury and eight sites in Muskoka-Haliburton ca. 225 km southeast of Sudbury. Comparisons were made between data collected before and after October 1978 when smelter operations were shut down due to strikes. They concluded that the bulk deposition of acidity, sulfate and total Cu at Muskoka-Haliburton did not significantly decrease during the shutdown supporting the view that at least for H^+ and $SO_4^=$ long range transport from many sources dominate the local deposition. At the Sudbury area (within 12 km of the source), however, they determined that sulfate decreased significantly (5-50%) during the shutdown period; for Cu and Ni the decrease in deposition was estimated to more than two orders of magnitude.

Remote sensing of the SO_2 plume at Sudbury in addition to conventional wet deposition measurements were employed by Millan et al. (1982). Total sulfur wet deposition in the near field agreed with that of previous studies, although the SO_2 deposition "plume" appeared at times displaced away from the sulfate and pH plumes, possibly a result of lowered solubilty of SO_2 from the increased acidity of the central plume, wind shear, or low-level source effects. Another Sudbury study (Lusis et al.,

1983) involved the measurement of scavenging rates of sulfur and trace metals from the smelter plume during the fall of 1980 and 1981. Bulk collectors were used on a precipitation event basis and deployed along two arcs, 14 km and 24 km downwind of the smelter. Most of the sampled storms were frontal in nature. For trace metals, despite differences in their particle size distributions comparable scavenging coefficients were observed, probably, due to in-cloud modification of the emitted particulate matter. For sulfur the scavenging rate was an order of magnitude less because of the fact that, within the acidic environment of the plume, little SO_2 (which makes up ca. 99% of the emitted sulfur) is dissolved in rain or cloud drops and removed by precipitation.

A smelter in the state of Washington was the apparent major source of excess pollutants measured in the Puget Sound area by Larson et al. (1975); the removal rate estimated for sulfur was comparable to that for Sudbury and most power plant studies. Mobile rain and snow sampling was undertaken around a sour gas processing plant in Central Alberta (Summers and Hitchon, 1973). They deduced that 30-45% of the sulfur emitted was removed during summer convective storms within 40 km, but less than 2% during the winter.

A wetfall chemistry study employing sequential precipitation samplers was undertaken by Pratt et al. (1983) at seven sites clustered within 40 km of each other in the vicinity of a coal burning plant in central Minnesota. This plant is located in a rural area 50 km northwest of Minneapolis/St. Paul. Sampling was undertaken during the summers of 1977 through 1980 and analyses involved pH and major ions. In this publication no effort was made to relate measurements to this local

source. Instead, the data were subjected to statistical investigations which demonstrated the absence of a correlation between H^+ and either $SO_4^=$ or NO_3^-. It was argued that weak acids contributed most of the H^+ due to alkaline dust, agricultural activities, and long range transport from distant pollutant sources.

SECTION 3

AREA SOURCES

In studying the impact of local sources on acid wet deposition it is customary to separate these sources into point and area sources. Area sources are usually urban and industrial centers. A fundamental distinction between the two types is the influence of the source on the local meteorology. Point sources rarely affect the local meteorology; area sources, on the other hand, are of sufficient size to significantly affect the local climate and meteorology. This is due to changes in surface roughness influencing the dispersion mechanisms, different radiational responses and the inputs of heat and pollutants at different heights impacting local and downwind cloudiness and precipitation patterns (AMS, 1981). This "weather modification" effect figures prominently in several aspects of the wet deposition and often necessitates a different experimental approach compared with the point source studies. Point source plumes are generally easy to locate and often "controlled" type experiments may be attempted since emissions can be easily monitored and detailed airborne and groundlevel measurements in a limited region of space may provide an adequate picture of the transformation processes (Gillani et al., 1978, 1981; Forrest et al., 1981) and the subsequent scavenging characteristics.

Apart from the "weather modification" effect mentioned above, area sources are also characterized by a complex and often intractable mix of pollutants derived from the wide variety of transportation, industrial, and residential activities on the urban scale. The complexity is com-

pounded by the temporal variability in emissions (by time of day, day of the week, season of the year, etc.). Since point sources are usually coal- or oil-fired power plants, sulfur oxides (SO_x) are their dominant pollutants followed by nitrogen oxides (NO_x). For area sources primary emissions of SO_x, NO_x, and hydrocarbons (HC) often compete for the dominant role with significant differences from one source area to another; even for the same source the dominant pollutant may depend on the time of day, season, etc. Knowledge of the magnitude and variability of urban emissions becomes an important prerequisite to successfully studying wet deposition on the urban scale.

It is important to identify the two distinct length scales associated with urban wet deposition. The first is the scale of the actual urban area. The importance of that pertains primarily to materials damage considerations since the density of materials at risk is highest within urban areas. It may be that dry deposition (i.e. air quality) may be considerably more important than wet deposition for materials damage. One facet of wet deposition, fog and dew (Cadle, 1984) may be also important in the urban environment due to accelerated oxidation of SO_2 to H_2SO_4 because of Mn catalysis (Penkett et al., 1979). Generally, however, wet deposition in the urban setting will be dominated by below cloud scavenging with variable net effects. The second length scale is the suburban-rural one which defines the extent to which the urban plume markedly impacts the wet deposition above regional background. This scale may indeed approach 100 km often because the urban plume with some downwind travel could mix thoroughly and may become incorporated into

clouds thus promoting faster acid-forming reactions. Identifying this second length scale is an important goal of source-receptor investigations particularly on the eastern coast of the U.S. and Canada where sensitive receptors are proximate to urban and industrial centers.

Literature addressing urban wet deposition is comparable, in quantity and quality, to that addressing wet deposition around point sources. There is a general paucity of relevant wet deposition data and several of the relevant publications have often relied on limited observations. There are two major field efforts which have attempted to quantify the urban source influence on downwind wet deposition in the U.S.: the wetfall chemistry studies around St. Louis (Hales and Dana, 1979b) which concentrated on summer convective storms and the Philadelphia field effort (Patrinos and Brown, 1984) which addressed frontal wintertime precipitation. Both studies concluded that contrary to the point source results, urban area emissions significantly impact the quality of precipitation on the suburban-rural scale. This is true for both convective and frontal meteorological situations and indeed a significant fraction of the emitted urban pollutants are deposited within 50 km of the urban center. Details on both studies will be given later.

The city of Uppsala in Sweden has been the focus of several early investigations of wet deposition. It is a moderately sized city (population 100,000) which is roughly circular in shape (radius ca. 7 km) and is in a relatively flat area with very few other pollution sources within a 60 km radius. One controversial aspect of this study is the nature of the urban emissions; ca. 65% of the SO_2 emissions originate at a 40m stack of a district heating station. Most of the remainder comes from an

additional 12 central heating refuse-burning facilities. Studies at Uppsala are, therefore, more hybrid, a combination of point and area sources, and not directly comparable to the studies around the large urban centers of the U.S. Andersson (1969) sampled monthly deposition (both wet and dry inputs) with a network of 24 stations in an area of ca. 400 km^2 surrounding Uppsala to a distance of ca. 40 km during July to October 1962. Sites within 4 km of the city center were considered urban; beyond 4 km they were considered rural. At an addditional 3 sites precipitation was sampled on a daily basis. Samples were analyzed for pH conductivity, Cl^-, Na^+, K^+, Ca^{2+} and total S. Urban sites showned significantly higher Ca^{2+}, Cl^-, and S levels; although some of the excess was due to dry deposition, wet deposition was considered largely responsible. These results appeared to support the claims by Stevenson (1968) who based his conclusions on data over the British Isles and Eire during a six-year period. In both these studies acidity did not show a definite pattern perhaps due to the conflicting influences of Ca^{2+} and S. Andersson attributed the urban effect to below cloud scavenging. Rhode (1970) conducted a simple analysis during a 12-day period of February 1969 by collecting fresh snow samples at 31 sites out to distances of 15 km from Uppsala. The sites were away from main roads and the samples were analyzed for total sulfur. Of the total emitted 240 tons of emitted sulfur less than 5% was deposited within 15 km. Högström (1974) studied the wet fallout of sulfurous pollutants emitted from Uppsala during rain or snow. A network of ca. 100 samplers was deployed at distances of 7, 20, 40, and 60 km from the city's center. Samples were collected on an event basis and analyzed from H^+ and sulfur. Based, primarily, on the data

from eight winter storms (during the period April, 1972 to April, 1973) Högström concluded that the characteristic scale of fallout appears in most cases to be in the range 50-100 km. He also found that sulfur was found to be deposited mostly as sulfate; a small amount was deposited as SO_2 fairly close to the source. Despite the fact that their study did not involve wet deposition measurements the work by Rodhe et al. (1972) is relevant in this discussion. They measured soot, particulate sulfur, and SO_2 in air on a daily basis at four remote coastal sites and at ten towns in southern Sweden during September to December 1969. They concluded that long range transport from source regions to the SE and SW was responsible for a significant percentage of the sulfur found at both the coastal and urban sites, particularly for sulfate; for soot and SO_2 local emissions dominated the urban sites. They also estimated a less than 5% SO_2 to sulfate transformation rate on the urban scale.

In the U.K. Davies (1976) studied the precipitation scavenging of SO_2 in the industrial region of Sheffield with significant iron and steel industries and a power station. Although it had been reported (Bielke and Georgii, 1968) that SO_2 contributes as much as 75% of the total sulfur in precipitation Davies expected that this figure would fluctuate widely. The study involved a single site with a sequential precipitation sampler with a recording raingage and hourly SO_2 measurements over a period of one year. Dissolved SO_2 was measured with the West and Gaeke (1956) method following the treatment of the rainfall samples with tetrachloromercurate (TCM). Results indicated that in absolute terms precipitation removes only a very small fraction of the emitted SO_2 in the industrial Don Valley as SO_2 washout even during the time of rainfall.

For individual rainfalls, the gradient of the washout-rainfall amount curve is smaller than the gradient of similar curves for sulfate. In general, the washout SO_2 concentration is quite low for light summer rains compared with light winter rains. Dissolved SO_2 values showed no obvious correlation with the majority of presumably important meteorological parameters emphasizing the inherent complexities of the processes in the industrial atmosphere. Following up on this study Davies (1979) examined SO_2 and sulfate in urban and rural precipitation in Norfolk, U.K. One sampling site was situated ca. 1 km west of Norwich (population ca. 150,000 with some light industry). The other site was 16 km west of Norwich, considered quite rural. Indeed most of Norfolk is quite rural with major sulfur sources situated more than 150 km to the SW. Sampling involved bottle funnel combinations (one with TCM for SO_2 fixing) as well as recording raingages. Atmospheric SO_2 concentrations were measured in the urban area and at a rural site. Monitoring was undertaken on an event basis between 10/77 and 8/78. Results are based on a total of 50 "urban-rural" pairs. Davies concluded that for the rural site ca. 15% of precipitation sulfate is derived from reactive scavenging of SO_2; for the urban site the corresponding percentage was 22%.

Another relevant study not involving wet deposition data is by Benarie (1976). It is based mostly on air quality data for one year from a station 37 km from the center of Paris, France. Based on existing emission inventories Benarie concluded that on an annual basis not more than half of the sulfur emissions leaves the 37 km radius boundary. Gaseous and particulate dry deposition were considered mainly responsible.

In North American, Liljestrand and Morgan (1981) examined the spatial variations of acid precipitation in southern California. Wet deposition data were collected at 9 sites in the Los Angeles basin of Southern California during the 1978-1979 hydrologic year. Sampling was performed on an event basis and samples were analyzed for all major ions, pH and conductivity. They determined that the major net acidity components H_2SO_4 and HNO_3 are partially neutralized by gaseous NH_3 and alkaline soil dust. Results indicate that the net acidity flux by wet deposition is ca. 15% of wet deposition in the northeastern U.S. (ca. 50% of that in the southeastern U.S.) due primarily to the arid climate and higher contributions from alkaline sources. Based on emission estimates the conclusions were that less than 2% of sulfur emissions and 1% of nitrogen emissions were scavenged on an annual basis in southern California. Nitric acid was the predominant acid however, particularly at the inland sites; H_2SO_4 showed maxima near the coast. Due to the distinctly different climatologies these results have dubious application for the northeastern U.S. and southeastern Canada where the emphasis of "effects" research has been placed.

In Nova Scotia, Shaw (1982) combined back trajectory calculations with analyses of air and precipitation quality to estimate the relative importance of different source areas. Data were collected during 1979 at a rural, coastal site ca. 25 km from the city of Halifax (population ca. 260,000). Aerosol sulfate was collected every third day (24h run) and precipitation with an automatic wetfall collector on an event basis. Chemical analyses of the precipitation samples involved only the major anions ($SO_4^=$, NO_3^-, Cl^-) and pH. Nitrate concentrations in the rainwater

were found to be 1/10 of the sulfate concentrations; it was speculated that the nitrate concentrations were low because of delays in the anal yses leading to biological degradation. Based on results from 56 individual storm events and the relevant surface wind data Shaw concluded that 50% of the annual wet deposition of H^+ and $SO_4^=$ within a 25 km radius of Halifax is due to the SO_2 Halifax emissions. These findings were supported further by data from the Dutch Settlement ca. 40 km to the northeast of Halifax. However, no effect of the city's emissions was felt at the monitoring sites of Truro and Kejimkujik ca. 100 km from Halifax. Shaw also confirmed the highly episodic nature of wet deposition of atmospheric acid: eight of the 56 storms contributed ca. 45% of the total annual wet deposition of $SO_4^=$; one storm, in fact, contributed ca. 13% of this total. It is reasonable to conclude that wet deposition in Atlantic Canada is more important that dry deposition. Shaw's results confirmed the findings of Watt et al. (1979) who attributed the high concentrations of H^+ and $SO_4^=$ in lake waters in the vicinity of Halifax to the urban emissions, and of Wiltshire (1979) who performed a sulfur budget for Nova Scotia concluding that 25% of the total deposition of sulfur in Nova Scotia is due to local emissions while 30% of local emissions are deposited within that province.

A comparison of "Lagrangian" meteorology with pH measurements around Washington, D.C., was undertaken by Draxler (1983). The pH measurements represented daily samples at 6 sites within a 15 km radius of Washington, D.C., during 1975. Approximately 75 sets of data were used in the analyses which were compared against the Lagrangian averages of temperature, rainfall, relative humidity, and normalized concentration from a multiple

source trajectory model. Draxler found that the most consistent acidic rainfall occured during an extended period from May to June when the flow was from the north. He concluded that the most important predictor of pH during the summer was the average rainfall along the trajectory. Based on this result he claimed that complex chemical source-receptor models were unnecessary for summer simulations; for the winter, results were ambiguous.

The hypothesis that local sources impact local wet deposition was tested by Dasch and Cadle (1984) and Dasch et al. (1984). Air and precipitation quality data were collected for a period of one year (June 81 to June 82) at two sites in S.E. Michigan, one in Warren which is ca. 7 km north of Detroit and the other ca. 50 km to the north of the first site. The Warren site was considered "urban" while the second site was considered "rural." Estimates of local emissions at the two sites showed a 300-fold increase in terms of SO_x (urban to rural), nine-fold increase in terms of NO_x and 56-fold for TSP. Precipitation was collected mostly on a daily basis. Dryfall was collected on a weekly basis from the "dry" buckets of the automatic collectors. Although air quality concentrations and consequently dry deposition, reflected higher values at the urban site wetfall chemistry was remarkably similar at both sites with only exceptions the Na^+ and Cl^- ions which showed higher concentrations at the urban site; precipitation samples were analyzed for all major ions, pH and conductivity. No evidence of local primary $SO_4^=$ was evident for both winter and summer rainfall. These results are generally at odds with most other urban deposition studies and underline the inherent difficulty of studying wet deposition on the urban scale with a limited number of

sites. It is conceivable that there was such a predominant transport during the sampled events that the effect of the urban plume was not detected at either site. Furthermore, the "urban" site may have been too close to the urban sources with below cloud scavenging being the only contribution to its wetfall chemistry.

The METROMEX study (AMS, 1981) and the RAPS effort (Schiermeier, 1978) were the first comprehensive field endeavors to investigate all aspects of the urban influence on meteorology, air quality and deposition. St. Louis, Missouri, was chosen as the focus; it is a continental city of negligble topographic relief with ca. 2.3 million people in the metropolitan area and substantial industrial activity. The wet deposition efforts concentrated mostly on the summer periods of 1972 and 1973 (Hales and Dana, 1979b). The primary objective was to assess the effectiveness of convective storms in removing urban pollutants and to provide a data base for scavenging model development. The network employed ca. 60 event-type samplers around St. Louis with different configurations during 1972 and 1973. Results are based on ca. 12 convective precipitation events; the samples were analyzed for most inorganic nonmetallic species. Hales and Dana concluded that precipitation scavenging is a highly efficient removal mechanism since the quantities of rainborne material ($SO_4^=$ and NO_3^-) deposited on the network downwind of the urban area because of the urban plume are comparable to the urban pollution burden (for SO_x and NO_x). Much of the observed rainborne $SO_4^=$ and NO_3^- appears to have been incorporated into the rain by scavenging of gaseous precursors. It may be that rapid oxidation of SO_2 to sulfate occurs in cloud systems in warm, polluted environments and leads to the observed

seasonal trends in $SO_4^=$ levels. The St. Louis wet deposition pattern showed a definite lack of organization in the H^+ patterns and poor correlations between H^+ and $SO_4^=$ and H^+ and NO_3^- ostensibly the consequence of the competing effects of NH_4^+ and the more abundant metallic cations. The Hales and Dana results appeared to contrast the conclusions of Scott and Laulainen (1978) whose analysis of winter-storm scavenging data from Michigan suggest [in concordance with Scott (1978)] that direct nucleation of cloud droplets by particulate $SO_4^=$ is the principal mechanism for scavenging. However, there are important differences between the two sets of results. For example, temperatures during the St. Louis experiments were 30°C warmer than the Michigan ones; increased photochemical activity during the St. Louis storms would produce substantial amounts of oxidants (O_3 and H_2O_2) which contribute to the reactivity of the scavenging mechanism. Furthermore the urban environment is most likely richer in catalytic trace metals which accelerate certain oxidation reactions. Regarding the deposition of nitrate, results disagree, in general, with those of individual power plants possibly because of faster formation of soluble products such as nitric acid. Even though the origin of nitric acid is suspected to be photochemical observed patterns for both day and night storms suggest other potential pathways to the nitric acid production (Richards, 1983).

Examining the relationships between measured sulfate concentrations in air and rain in St. Louis on four days (during the summers of 1974 and 1975) Bridgman (1984) disputed the reactive scavenging claims of Hales and Dana. Bridgman detected considerable variability in both media

across the mesoscale network. Aerosol $SO_4^=$ varied by a factor of up to nine from stations directly affected by point source emissions to those most unaffected. Spatial variability of normalized sulfate in rain is on the order of a factor of 3, although at occasional individual sites $SO_4^=$ concentrations were much higher. In three of the four cases, sulfate concentration patterns in air and rainwater were similar, and consistent with wind direction and location of potential sources. The similarity in patterns of $SO_4^=$ in air and rain and the location of the highest concentrations of both close to the major sources of SO_x emissions indicated to Bridgman that nucleation must be the major cause of sulfate scavenging with sub-cloud impaction perhaps having a small role.

Associated with METROMEX was the study by Gatz (1980) who examined wet deposition data from ten convective rain events during the summers of 72, 74, and 75. Approximately 85 collectors covering 2200 km^2 around St. Louis were analyzed for Li, Na, Mg, K, Ca, Fe, Zn, Cd, and sulfate (soluble and insoluble). Factor analysis was applied to these mesoscale data and results showed that deposition patterns grouped consistently into four main types (1) soluble soil elements, (2) insoluble soil elements, (3) soluble pollutant elements, and (4) insoluble pollutant elements. Gatz concluded that the differences between soil element and pollutant deposition patterns reflect different source regions while the differences between soluble and insoluble element deposition patterns reflect differences in scavenging and/or precipitation formation processes.

SECTION 4

THE PHILADELPHIA FIELD STUDY

BACKGROUND

The Philadelphia field study was conceived partly in response to the growing controversy regarding the impact of large area sources on local wetfall chemistry (Spaite and Szabo, 1982). The only other study similar in scope and objectives was the one conducted during METROMEX (Hales and Dana, 1979b) at St. Louis, during the early 1970's before the emergence of widespread awareness of the "acid rain" problem. The conclusions of the St. Louis study were limited to summertime convective storms in the Midwest. The geographical limitation is not considered important; it is felt that insofar as the meteorological effect on wet deposition for convective storms is concerned, the results could be accepted for area sources in the eastern U.S. and Canada. The "data gap" existed primarily for frontal and primarily nonconvective storms which are responsible for the largest fraction of wet deposition, particularly in the Northeast [according to one estimate, greater than 60% (Raynor and Hayes, 1982)]. Available estimates of the importance of area sources on local wet deposition have been based on spatially limited data (Dasch and Cadle, 1984; Shaw, 1982) with conflicting conclusions. More complete data are available from Europe, particularly Sweden (Högström, 1974), but there is serious doubt whether these results are relevant to the U.S. since the Swedish area sources are considerably smaller and the climatology somewhat different.

Philadelphia was chosen as the test site because it is a reasonably large city (population ca. 2.5 million) with considerable industrial activity along the Delaware Valley. It is, also, sufficiently inland to avoid the complications of a mostly coastal city (e.g. New York or Boston). Philadelphia has been the target of several air quality studies [e.g. the Philadelphia Aerosol Field Study (PAFS)] and consequently has contributed to a reasonable emissions inventory, perhaps better on the average than for most other cities. A possible complication is the position of Philadelphia in the center of the heavily urbanized and industrialized "Northeast Corridor" (from Washington, D.C. to Boston) with possible multiple urban plume interactions. As it developed this complication was not a serious one because of fortuitous meteorological conditions during the sampled storms.

The field study was geared toward the sampling of frontal and primarily nonconvective storms and was divided into two parts: an exploratory phase during the fall, 1983, period and the main field effort during March and April of 1984. The primary objective was to sample a sufficient number of storms in order to provide an adequate data base for a quantitative assessment of the area sources impact on mesoscale wet deposition.

THE EXPLORATORY PHASE AND QUALITY ASSURANCE

The exploratory phase of the field study was undertaken to investigate the suitability of the candidate sampling sites and the density of the sampling network, to establish a comprehensive quality assurance and quality control (QA/QC) program, and to test the field study logistics. Approximately 40 sites were selected on both sides of the Delaware Valley around Philadelphia and within a 60 km distance from the river (Fig. 1).

Figure 1

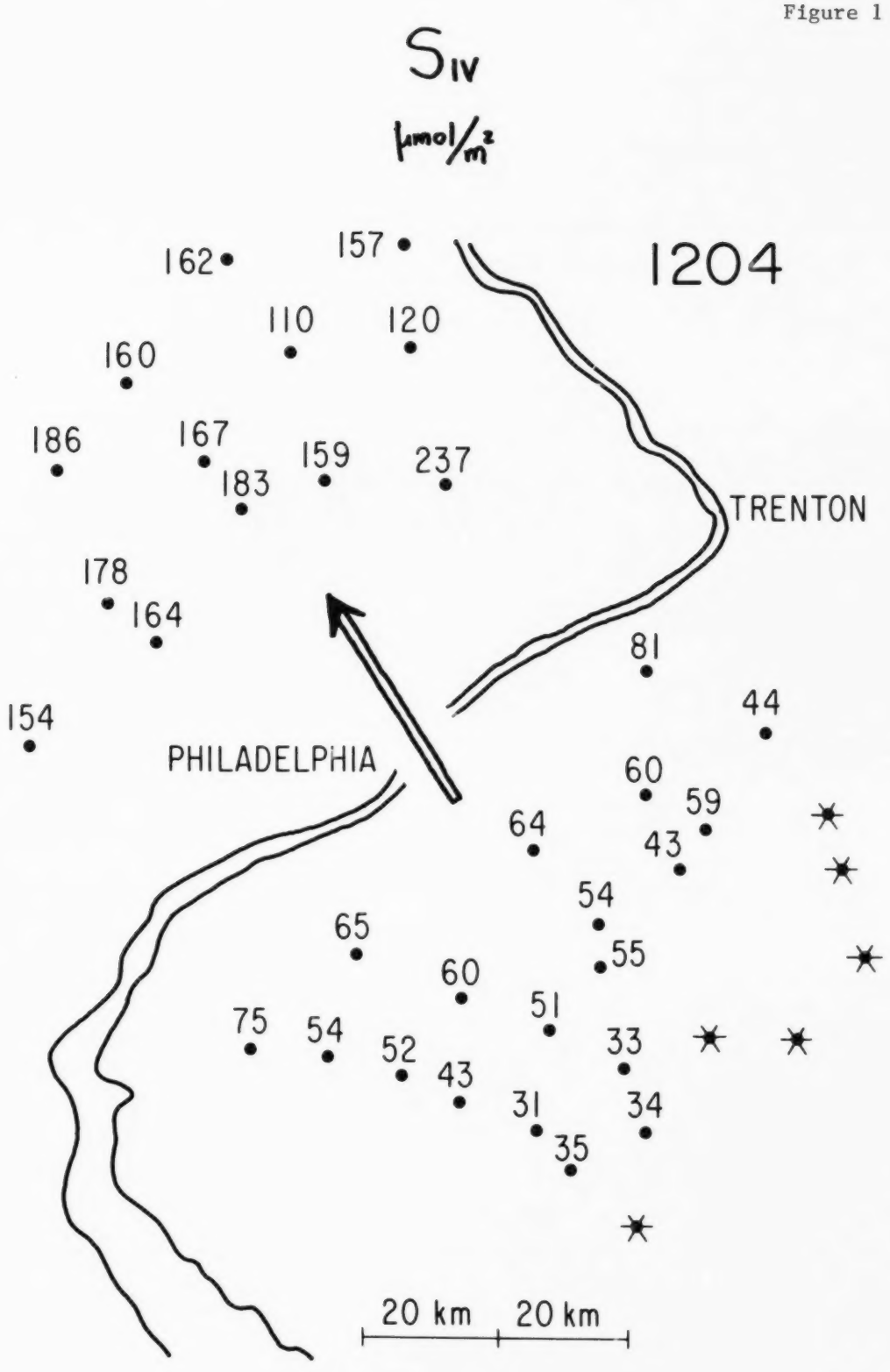

SIV
μmol/m²
1204
162
157
110
120
160
186
167
159
237
183
TRENTON
178
164
81
154
44
PHILADELPHIA
60
59
64
43
54
65
55
60
51
75
54
52
33
43
31
34
35
20 km
20 km

TABLE 2.

Storm	Period	Precipitation Type	Precipitation Characteristics	Weather System
1111	1230 EST 11/10/83 to 2200 EST 11/10/83	Rain, steady and stable	Fairly uniform spatially, heavier in NJ, average approx. 3.4 cm.	Overrunning a high in New England. Low pressure system moving up the coast.
1204	0300 EST 12/4/83 to 1000 EST 12/4/83	Rain, steady and stable	Uniform spatially, slightly heavier in NJ, average approx. 3.3 cm.	Overrunning a high in New England. Low pressure system moving up the coast.
0306	0530 EST 3/5/84 to 0300 EST 3/6/84	Started as snow, stable, continuous	Spatially uniform, average amount approx. 2 cm.	Overrunning an advancing W-E warm from the south.
0314	0400 EST 3/13/84 to 0000 EST 3/14/84	Started as snow, stable, continuous	Fairly uniform spatially, heavier in NJ, average approx. 4.3 cm.	Overrunning a cold high in New England. Formation of secondary low.
0321	0700 EST 3/21/84 to 1600 EST 3/21/84	Rain, convective, intermittent showers	Nonuniform spatially, average in NJ approx. 0.3 cm, average in PA approx. 0.8 cm.	Overrunning an advancing W-E warm from the south.
0326	0700 EST 3/25/84 to 0000 EST 3/26/84	Rain, light but steady, stable	Nonuniform spatially, average in NJ approx. 0.3 cm, average in PA approx. 0.8 cm.	Low pressure system moved out to sea, south of network.
0329	2000 EST 3/27/84 to 2000 EST 3/29/84	Light rain initially then heavy, some snow to light rain stable with imbedded convection	Spatially uniform, average approx. 5.7 cm.	Deep low formed in the southeast. Tracked to the northeast, moved out to sea off the NJ coast.
0405	0830 EST 4/4/84 to 1100 EST 4/5/84	Rain, fairly steady, stable	Fairly uniform spatially, average approx. 5.8 cm.	Overrunning a warm W-E warm front attached to low which passed just west of network.

For the exploratory phase the samplers were simple bottle-funnel combinations (B samplers) which were deployed a short time before the onset of precipitation and collected shortly after the cessation of precipitation. Deployment and collection timing was, therefore, crucial in minimizing dry fall contamination; these activities were closely coordinated with the National Weather Service (NWS) forecast office in Philadelphia.

The exploratory phase involved the sampling of two precipitation events during the fall of 1983. Table 2 presents the important meteorological features of these storms. Emphasis was placed on cyclonic-type storms with minimum convective activity and as it developed the selection was quite good.

A comprehensive QA/QC program was developed for this study (Patrinos, 1983); it covered all aspects: the sampling instruments, the sampling procedures and the chemical analyses of the collected rainfall samples. The development of rigorous and scientifically defensible QA/QC standards was an important goal of the Philadelphia study because of the realization that QA/QC shortcomings had compromised a number of previous wet deposition studies.

Interim QA/QC results from the field study have been satisfactory (Patrinos, 1984). Several aspects of the QA/QC program are presented in order to highlight the importance of QA/QC in wetfall chemistry studies.

- The wetfall chemistry automatic wetfall collectors (A samplers), which were used during the main field study, have two sensitivity controls. One establishes the intensity of the signal which triggers the opening sequence, the other controls the

degree of heating of the sensor head. The first controls the degree of moisture sensing; if the setting is too sensitive, the instrument will respond too quickly, potentially exposing the samples to dry deposition. On the other hand, if it is not sensitive enough, it may miss the first part of the rain which may contain important chemical information. The second determines the speed with which the collector responds to the cessation of rainfall. Both sensitivity controls should be judiciously set for the "typical" circumstances expected during the field operations. What is perhaps more important is that all wetfall collectors used in the field be uniformly adapted to identical sensitivities. This was accomplished during a two-month period (December 1983 to January 1984) when all collectors were deployed side-by-side and their behavior monitored continuously during real and simulated rain events. This allowed the periodic adjustments of the sensitivities to accomplish a uniformly acceptable performance by all collectors prior to deployment.

- Rainfall samples were collected into polyethylene bottle-funnel combinations which fit in the standard 13-L bucket of the automatic wetfall collector. Thus, each site was represented by two independent samples and provided an assurance against inadvertent contamination due to operator error or fugitive debris. An advantage of the use of the bottle-funnel combination is the minimization of escape of dissolved gases in the precipitation samples due to the narrow funnel stems.

- Each automatic wetfall collector was collocated with a raingage geared for daily recording for the accurate estimation of beginning and ending times of precipitation and of rainfall rates. The presence of the raingages was a check for the collection efficiency of the automatic wetfall collectors. Collection efficiency was often doublechecked with the deployment of B samplers at several A sites. In fact, during the main field study a B network was intertwined with the A net work. Apart from increasing the sampling density this provided an estimate of dryfall's contribution to the wetfall chemistry.
- The chemical analyses of the collected rainfall samples represent one of the most important and costly activities of the field effort. The QA/QC program involved the use of two independent analytical chemistry laboratories (BNL and PNL), use of dynamic blanks (standards) from both laboratories to be used as dummy rainfall samples and blind analyses of parts of the same rainfall samples from several sites by both laboratories. Upon collection, rainfall samples were rapidly analyzed at a field laboratory for pH and conductivity after aliquots were taken for TCM fixing (for dissolved SO_2 estimation).

THE MAIN FIELD STUDY AND GENERAL RESULTS

The main field effort was conducted during March and April of 1984. Most of the sites used during the exploratory phase were also used during the main field effort. Twenty four of the ca. 40 sites were designated as A sites; there were ca. 14 B sites. Sampling procedures and operat_

ional details are presented elsewhere (Patrinos et al., 1983; Patrinos, 1983; Dana et al., 1984; Patrinos and Brown, 1984). Nine precipitation events were sampled during the main two-month experimental period. With two exceptions these events represent the period's total wet deposition. The exceptions were, a snowstorm on March 8 and a number of convective showers which occurred during the early part of the week of April 16. The network was not activated during those times because of sampling problems associated with entirely frozen precipitation and because the showers were forecasted as too scattered. Summaries of the important meteorological features of these storms are presented in Table 2. As with the fall 1983 period, the majority of the storms were primarily nonconvective in nature and were associated with overrunning. This is typical of a dominant type of precipitation in the Northeast for this period: strong cyclonic systems forming in the southeastern United States and travelling to the northeast. A frequent occurrence is the development of a secondary low pressure system off the coast of Virginia which tracks to the north; this is particularly the case when the main cyclonic system is located further inland. The meteorological characteristics of this storm are responsible for the prevailing southeast to northwest transport configuration during most of the sampled storms.

According to published estimates of source emissions (Benkovitz, 1980) and more current information from the air quality monitoring agencies of the city of Philadelphia and the states of New Jersey (NJ) and Pennsylvania (PA) approximately 80% of the SO_x, NO_x, and HC emissions in the sampling region occur within 20 km of Delaware river. Consequently

ional details are presented elsewhere (Patrinos et al., 1983; Patrinos, 1983; Dana et al., 1984; Patrinos and Brown, 1984). Nine precipitation events were sampled during the main two-month experimental period. With two exceptions these events represent the period's total wet deposition. The exceptions were, a snowstorm on March 8 and a number of convective showers which occurred during the early part of the week of April 16. The network was not activated during those times because of sampling problems associated with entirely frozen precipitation and because the showers were forecasted as too scattered. Summaries of the important meteorological features of these storms are presented in Table 2. As with the fall 1983 period, the majority of the storms were primarily nonconvective in nature and were associated with overrunning. This is typical of a dominant type of precipitation in the Northeast for this period: strong cyclonic systems forming in the southeastern United States and travelling to the northeast. A frequent occurrence is the development of a secondary low pressure system off the coast of Virginia which tracks to the north; this is particularly the case when the main cyclonic system is located further inland. The meteorological characteristics of this storm are responsible for the prevailing southeast to northwest transport configuration during most of the sampled storms.

According to published estimates of source emissions (Benkovitz, 1980) and more current information from the air quality monitoring agencies of the city of Philadelphia and the states of New Jersey (NJ) and Pennsylvania (PA) approximately 80% of the SO_x, NO_x, and HC emissions in the sampling region occur within 20 km of Delaware river. Consequently

the prevailing transport configuration caused the NJ sector of the network to be the upwind (or control) region while the PA sector was the downwind (or target) region of the network. The determination of the prevailing transport was made primarily on the basis of data supplied by the NWS. Four of the sampled eleven storms (from both the exploratory and main periods) were considered the "best" in establishing the "source receptor" relationship for the following reasons: clear start and end in precipitation, steady transport during the precipitation, fairly uniform (spatially) and sufficient rainfall amounts, minimum convective activity and satisfactory QA performance. These storms were 1111, 1204, 0405, and 0424. Storm 0314 was also quite useful although the transport veered ca. 180° towards the end of precipitation. Continuously veering transport also compromised storm 0306 making a control-target delineation impossible. The latter two storms would have been extremely valuable if sequential precipitation sampling was implemented. Storms 0414 and 0415 are of limited value because, despite steady transport, they were part of a stagnant weather system with convective activity and intermittent periods of light rain. Storms 0321 and 0326 shed no light on the impact of urban emissions because of very low rainfall amounts on the NJ and PA sectors of the network respectively. Storm 0329 was compromised by poor QA performance; this was an intense coastal storms with high winds resulting in widespread instrument malfunctions (power losses, tipped sampling buckets, contaminated samples, etc.) and a limited number of valid data.

Table 3 presents the statistics of deposition of the various species for the various storms. The unit of deposition is in $\mu mol/m^2$. Sample

Table 3. Statistical Summary of Deposition Data. The depicted three numbers per entry a-b-c are: a = number of sites, b = mean, c = standard deviation. The units are mm for rainfall volume and umol/m^2 for chemical species.

Storm	V[a]	H_F^+[b]	H_L^+[c]	NO_3^-	$SO_4^=$	NH_4^+	Na^+	Cl^-	Ca^{++}[d]
1111	B(NJ) 25-41.4-7.2	24-732-120	24-860-143	24-233-41	24-346-80	24-171-24	24-275-112	24-378-157	24-49-9
	B(PA) 13-23.6-4.1	13-1189-240	13-1331-281	13-716-153	13-492-89	13-285-117	13-92-18	13-146-30	13-35-15
1204	B(NJ) 25-35.2-3.5	25-823-70	25-908-74	25-285-28	25-305-58	25-85-17	25-562-393	25-633-412	25-47-4
	B(PA) 14-29.8-1.5	14-753-61	14-867-76	11-237-25	14-298-116	14-122-67	14-93-46	14-154-46	14-40-2
0306	A(NJ) 12-20.8-3.6	12-1599-88	12-1939-135	12-1032-88	12-766-61	12-622-76	12-162-35	12-202-28	12-54-11
	A(PA) 8-21.6-23	8-1637-203	8-2119-377	8-893-85	8-759-117	8-584-118	8-69-20	8-139-38	8-44-19
	B(NJ) 13-22.2-3.8	13-1745-112	13-1618-166	13-949-73	13-826-63	13-496-54	13-173-51	13-216-39	13-66-15
	B(PA) 6-22.5-1.5	6-1812-167	6-1759-278	6-929-60	6-839-112	6-472-46	6-68-22	6-145-39	6-65-23
0314	A(NJ) 9-47.6-7.0	9-761-102	9-1049-143	9-212-53	9-365-54	9-114-31	9-221-79	9-263-89	9-184-58
	A(PA) 10-39.6-8.3	10-846-102	10-1241-145	10-306-60	10-439-60	10-91-39	10-66-29	10-109-35	10-209-1
	B(NJ) 12-52.1-6.9	12-742-92	12-1294-159	12-255-48	12-496-82	12-168-39	12-313-137	12-346-150	12-279-6
	B(PA) 2-38.4-12.8	2-774-82	2-1505-47	2-348-55	2-552-96	2-189-116	2-194-136	2-194-109	2-677-24
0405	A(NJ) 12-52-6.8	12-1548-316	11-1951-406	12-313-51	12-1019-174	12-313-43	12-1910-528	12-2221-546	12-85-16
	A(PA) 11-80.2-10.3	11-2454-345	9-2969-383	10-906-142	10-1351-168	10-553-179	10-1053-302	10-1236-570	10-118-1
PNL[e]	B(NJ) 12-52.5-6.7	12-1528-334	9-2017-322	9-316-55	9-1087-212	9-322-36	9-2035-537	9-2155-565	9-91-15
	B(PA)								
	A(NJ)		f	12-313-63	12-919-211	12-370-55	12-1966-593	12-1920-687	12-48-9
	A(PA)		f	11-907-170	11-1291-207	11-660-203	11-1244-546	11-1376-530	11-71-14
BNL[e]	B(NJ)		f	12-337-118	12-947-232	12-350-115	12-1894-672	12-2115-781	12-46-6
	B(PA)								
0424	A(NJ) 11-15.2-3.3	11-333-61	f	11-107-36	11-135-34	11-60-14	11-86-50	11-170-79	11-20-4
	A(PA) 9-11.8-1.4	9-575-128	f	9-252-66	9-251-51	9-119-45	9-34-9	9-138-33	9-35-11
	B(NJ) 14-18.5-3.5	12-440-139	f	12-156-47.4	12-191-63	12-89-30	12-134-78	12-259-111	12-32-7
	B(PA) 5-13.5-2.1	4-689-84	f	4-377-78	4-338-113	3-176-47	4-32-4	4-165-32	4-43-12
0414	A(NJ) 5-2.5-2	9-221-76	5-243-109	5-138-61	5-95-43	5-55-44	5-128-80	5-133-78	5-35-31
	A(PA) 4-4.5-0.6	7-199-75	4-420-109	4-332-75	4-267-24	4-288-29	4-60-28	4-73-45	4-75-18

Table 3. Statistical Summary of Deposition Data. The depicted three numbers per entry a-b-c are: a = number of sites, b = mean, c = standard deviation. The units are mm for rainfall volume and umol/m^2 for chemical species.

Storm	V[a]	H_F^{+}[b]	H_L^{+}[c]	NO_3^-	$SO_4^=$	NH_4^+	Na^+	Cl^-	Ca^{++}[d]
0415	A(NJ) 7-6.5-3.6	f	f	7-167-71	7-163-70	7-162-70	7-88-25	7-102-36	7-18-6
	A(PA) 9-3.9-0.9	f	f	7-189-38	7-133-25	7-113-26	7-33-9	7-43-16	7-10-3
	B(NJ) 6-8.2-4.4	f	5-510-231	5-219-80	5-228-66	5-228-92	4-147-43	5-168-53	3-33-15
	B(PA) 4-4.1-1.0	f	3-547-21	3-296-38	3-187-15	3-154-18	2-62-20	3-60-13	2-17-8

a Rainfall volume in mm derived from sample volumes
b From field pH
c From laboratory pH
d Many of the concentrations were below detection level (1.4 uM) Minimum detection level was used for deposition volumes, thus overestimating the high volume samples
e Samples were analyzed at BNL and PBL
f Imcomplete analyses

volumes are given in mm of rain. The first most important conclusion of the field study concerns the impact of fresh NO_x emissions on the production and deposition of nitric acid. If synoptic transport over the lowest kilometers of the atmosphere remains steady during the storm and the control-target distinction can be confidently made, target deposition of nitrate may increase by as much as 200% compared with control deposition. This was the case for 1111 and 0405; storm 1111 in fact registered the highest target-control increase both in absolute and relative terms. The increase for 0424 was somewhat less (ca. 140%), while for 0314 the veering transport during the tail end of the storm may have diluted the final impact (ca. 50%). Veering transport is considered responsible for the uniform pattern of 0306 while for 0414 and 0415 no firm conclusions can be reached because of less than ideal sampling circumstances and insufficient rainfall amounts. Storm 1204 is a special case as will be described later. Table 3 distinguishes between the results obtained from the A and B networks; it also presents results of duplicate analyses at BNL and PNL.

It is important to emphasize the difficulties of using event-type sampling to estimate longer-term (seasonal and annual) differences and trends since a considerable fraction of total wet deposition may be associated with less organized weather systems causing long, intermittent, and spatially inhomogeneous rain events. Nevertheless, it is felt that only event-type sampling and perhaps sequential within-event sampling can provide the comprehensive information blocks required to determine the impact of local sources. Such information blocks, together with a firm knowledge of precipitation climatology, may provide the necessary

assessment of impact on longer time scales. The importance of event-type sampling is highlighted with storm 1204 which contrasted the majority of the sampled storms. This storm despite the remarkable meteorological similarities with 1111 showed no impact of the urban emissions on most ionic species; in fact, a target reduction in nitrate and total acidity was noted. However, this storm showed a widespread distribution of dissolved SO_2 gas (Fig. 1) and an over 200% target-control difference. Table 4 shows the statistics of dissolved SO_2 for the sampled storms. The dissolved SO_2 result for 1204 is particularly noteworthy because it is derived entirely on the basis of B samples and despite good deployment and collection timing some escape must have taken place. The seasonal dependence of dissolved SO_2 is in line with the published literature (Hales and Dana, 1979a; Dana, 1980; Dana, 1985).

Several explanations have been examined (Patrinos and Brown, 1984; Patrinos et al., 1984) regarding the unique features of storm 1204. It should be noted that the storm occurred on a Sunday morning with most of the rainfall ending before sunrise. Some of the considered explanations are presented:

- Despite apparent meteorological and transport similarities between 1204 and the other storms, subtle yet important synoptic and microphysical differences (cloud base height, vertical winds below clouds, cloud thickness, extent of mixing of surface layer air with air from aloft during precipitation formation, etc.) led to reduced SO_2 and NO_x incorporation into clouds and reduced conversion to H_2SO_4 and HNO_3 for 1204.

Figure 2

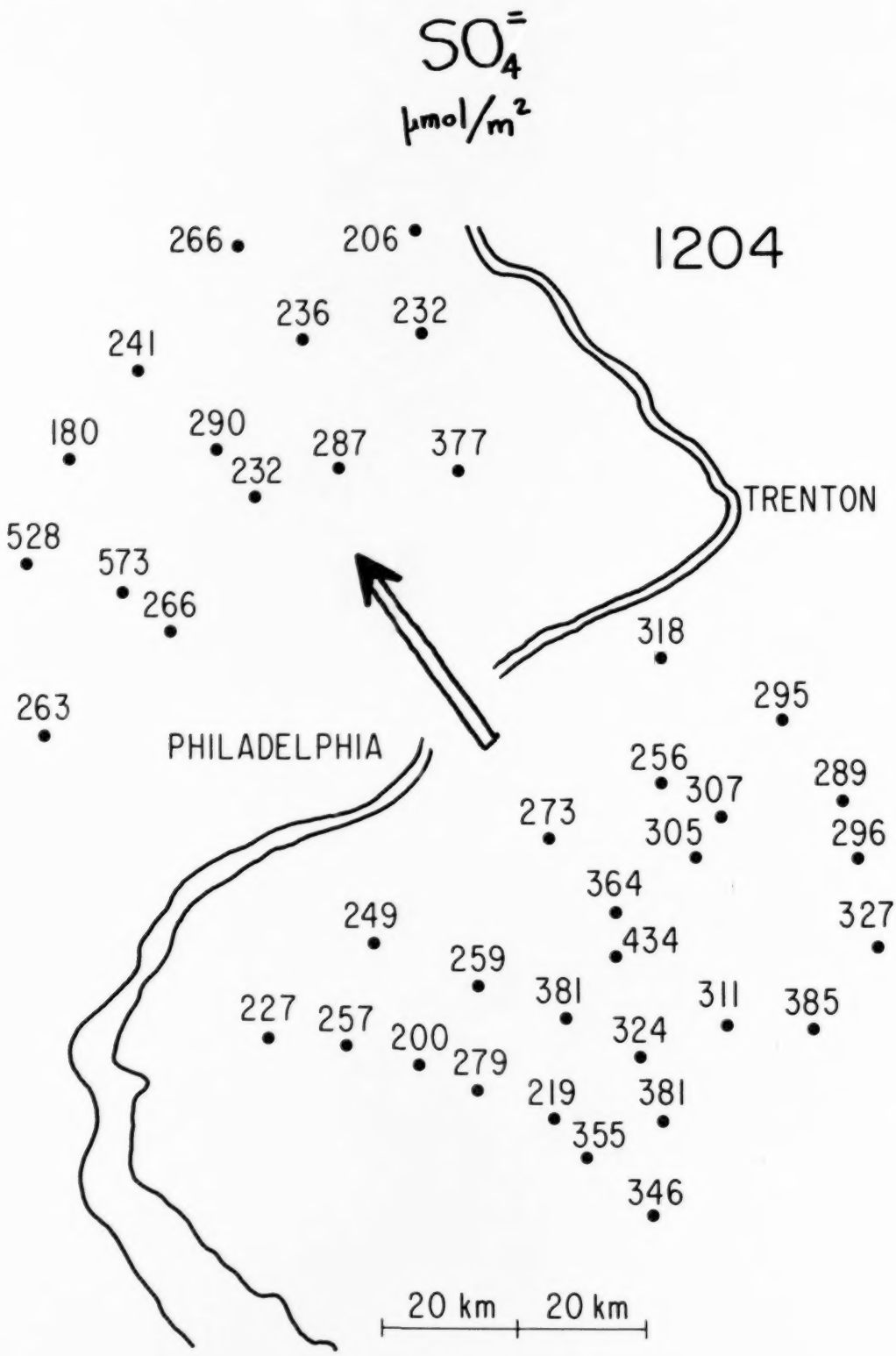

$SO_4^=$
μmol/m²
1204
TRENTON
PHILADELPHIA
266
206
236
232
241
180
290
287
377
232
528
573
266
263
318
295
256
307
289
273
305
296
364
249
327
434
259
381
311
385
227
257
200
324
279
219
381
355
346
20 km
20 km

Table 4. Dissolved SO_2 Deposition Data for Sampled Storms (unit: umol/m^2)

Storm		Sites[a]	Mean	Standard Deviation
1111	NJ	2	60	20
	PA	3	55	27
1204	NJ	25	47	15
	PA	13	164	31
0306	NJ	-	-	-
	PA	5[b]	51	18
0314	NJ	-	-	-
	PA	10	84	26
0326	NJ	13	66	12
	PA	c	c	c
0405	NJ	2	115	81
	PA	-	-	-

[a]Most samples were below detection level (1 uM); only samples with concentrations above detection level are given.

[b]Both A and B samples are used in the computations.

[c]Sample volumes in the PA sector were low but concentrations were similar to those on the NJ sector; dissolved SO_2 analyses for storm were performed at PNL.

° Weekday-weekend differences in emission rates leading to lower oxidation processes which are first order in SO_2 and NO_2. The occurrence of precipitation during 1204 coincided with the minimum in manufacturing and transportation emissions (EPA, 1982). Evidence of improved air quality near large cities during weekends has been shown for ozone (Cleveland and McRae, 1978; Cleveland and Graedel, 1979); it is reasonable to assume that the precursor pollutant mix emitted by the city may be reduced for a weekend storm leading to the absence of significant excess deposition in the target region. Although comparisons of air quality data from various local agencies for the various storms do not generally support this explanation, lower mixing heights for 1204 may have contributed to the observed similarities in air concentration patterns.

° In general terms, the concentrations of OH control the conversion of SO_2 and NO_2 below clouds; in-cloud conversions are controlled by H_2O_2 (Penkett et al., 1979; Schwartz, 1984). Hence, since both are driven by radical species

$$2HO_2 \dashrightarrow H_2O_2 + O_2$$

they occur more rapidly in the daytime. This is supported by the abundance of dissolved SO_2 for 1204. The nighttime conversion of NO_2 via reaction with ozone.

$$O_3 + NO_2 \dashrightarrow NO_3 + O_2$$

$$NO_3 + NO_2 \dashleftarrow\dashrightarrow N_2O_5$$

$$N_2O_5 + H_2O \dashrightarrow 2HNO_3$$

may, in fact, be occurring but at a substantially slower rate than the daytime OH reaction. Reduced ozone concentrations due to "weekend" effects may, also, be slowing the above sequence.

It is possible that all three causes may be synergistically responsible for the unique features of storm 1204. None of the storms of the March-April experimental period exhibited the exclusive characteristics of 1204 and, consequently, no further experimental support of an individual expanation can presently be pursued. At the same time, the exclusive nature of this storm may, from a statistical standpoint, deemphasize its importance in estimating longerterm assessments of local source contributions.

The impact of the urban and industrial emissions on the deposition of $SO_4^=$ appears less striking compared to the deposition of NO_3^-. The maximum target control increase was seen for storm 0424 which showed an ca. 90% rise. Among the others that showed an increase it averaged less than 50%. As mentioned earlier, storm 1204 exhibited a 240% increase in the deposition of dissolved SO_2; the presence of these unreacted SO_2 amounts in the rain may be another indication of the exhaustion of H_2O_2 in cloudwater which reduces the extent of SO_2 oxidation. The fact that no excess sulfate in the target area was seen for 1204 (Fig. 2) supports the hypothesis that primary sulfate emissions have a negligble contribution on downwind precipitation chemistry. After all, the suspected major sources of primary sulfates are residential boilers and would not have experienced the weekend emission reductions assumed for the manufacturing and transportation sources. Therefore, it is reasonable to conclude that whenever a target $SO_4^=$ excess is observed, it is mostly the result of rapid SO_2 to $SO_4=$ oxidation, particularly in the liquid phase.

Table 5. Estimates of NO_x and SO_x emission rates (in tons/year) along the Delaware Valley

	NO_x	SO_x
Point Sources	110,000	170,000
Areal Sources	140,000	40,000
Total Sources	250,000	210,000

The more substantial impact of the Valley emissions on NO_3^- rather than $SO_4^=$ can be rationalized on several grounds. NO_x are typically oxidized to nitrate more rapidly than SO_2 is oxidized to sulfate in the daytime (Spicer, 1982; Calvert and Stockwell, 1983; Platt et al., 1984) and NO_x oxidation potentially continues aloft at night while SO_2 oxidation typically shuts off. Furthermore, gaseous nitric acid is removed from the atmosphere much more rapidly than particulate sulfate, and some fine particle nitrates can volatilize to release nitric acid (Richards, 1983). The quantity and nature of NO_x vs. SO_x emissions may also promote a more vigorous HNO_3 production. This may be related to the more diffuse and lower-level manufacturing, refinery, and transportation emissions of NO_x compared to SO_2 emissions which may be dominated by a few elevated sources. The diffuse nature of the NO_x emissions may provide longer residence times, more efficient mixing with other pollutants and oxidants (Gorham et al., 1984) and generally greater availability for reaction and scavenging both in-cloud and below-cloud (Levine and Schwartz, 1982).

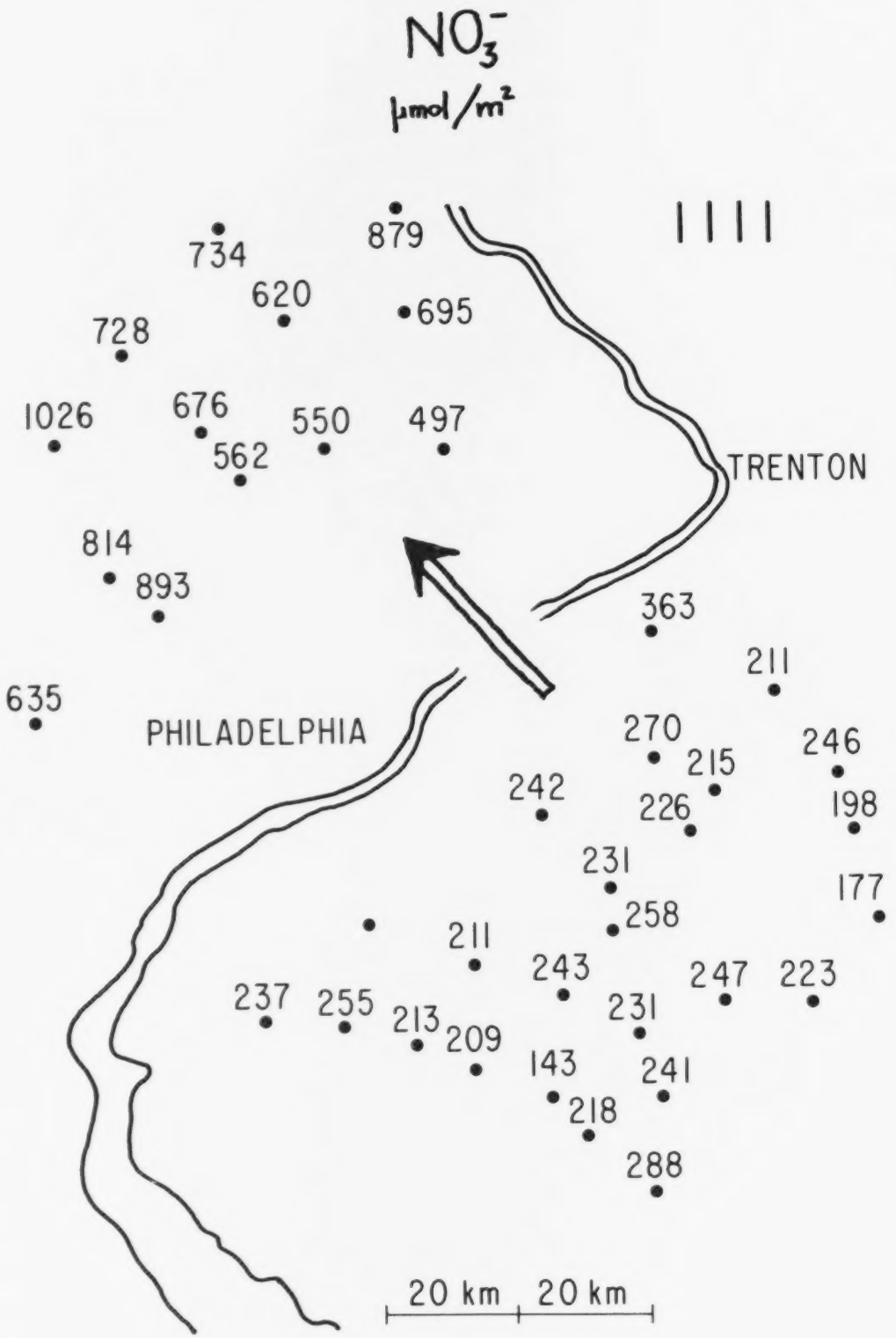
An attempt was made to estimate the relationship between the deposited excess NO_3^- and $SO_4^=$ for the various storms and the emitted NO_x and SO_x in the sampling region. The emission estimates are based on published information (Benkovitz, 1982) and data supplied by local agencies. It is unclear whether NO_x emissions from local refineries are accounted for; elevated NO_x levels downwind of refineries have been documented by several investigators (Sexton and Westberg, 1983; Parungo and Pueschel, 1980; Parungo et al., 1980). As mentioned earlier, 80% of all emissions in the sampling region occur within 20 km of the Delaware

River. Table 5 presents these estimates for both areal and point sources. Assuming uniform emission rates (from Table 5) and accounting for the period of rainfall, the ratio of deposited excess NO_3^- in the downwind sector to emitted NO_x is estimated to be ca. 50% for 1111, ca. 30% for 0405 and less than 10% for 0424 and 0314. For the corresponding sulfur estimates (dissolved SO_2 and $SO_4^=$), comparisons indicate ca. 20% for 1111, 1204, and 0405, and less than 10% for 0424 and 0314.

Storm 0424 showed a sizable target-control relative increase but a low excess deposition to emission ratio for both nitrogen and sulfur. Apart from the strong meteorological and transport similarities with 1204 there was a similarity with the time of occurrence as well. A considerable fraction of the 0424 rain occurred over a Sunday (in fact the Easter Sunday) evening to Monday morning and consequently some emissions (primarily manufacturing and transportation) may have been reduced during the early part of the storm compared with the average weekday values leading to the low excess deposition-to-emission ratios. Nevertheless, the sizable target-control relative increases of NO_3^- and $SO_4^=$ indicate that the similarities with 1204 did not extend to the supression of HNO_3 and H_2SO_4 production.

It is important to emphasize that for those cases with an increased target deposition of NO_3^-, the effect appears to increase with distance from the Delaware River, suggesting perhaps that the impact may indeed peak beyond the distance of 60 km which represents the domain of the sampling network. Figs. 3 and 4 present the deposition patterns for 1111 and 0405. This suggestion may have important implications regarding the

Figure 3


NO_3^-
μmol/m²
879
734
620
695
728
1026
676
550
497
562
TRENTON
814
893
363
211
635
PHILADELPHIA
270
246
215
242
226
198
231
177
258
211
243
247
223
237
255
213
231
209
143
241
218
288
20 km
20 km

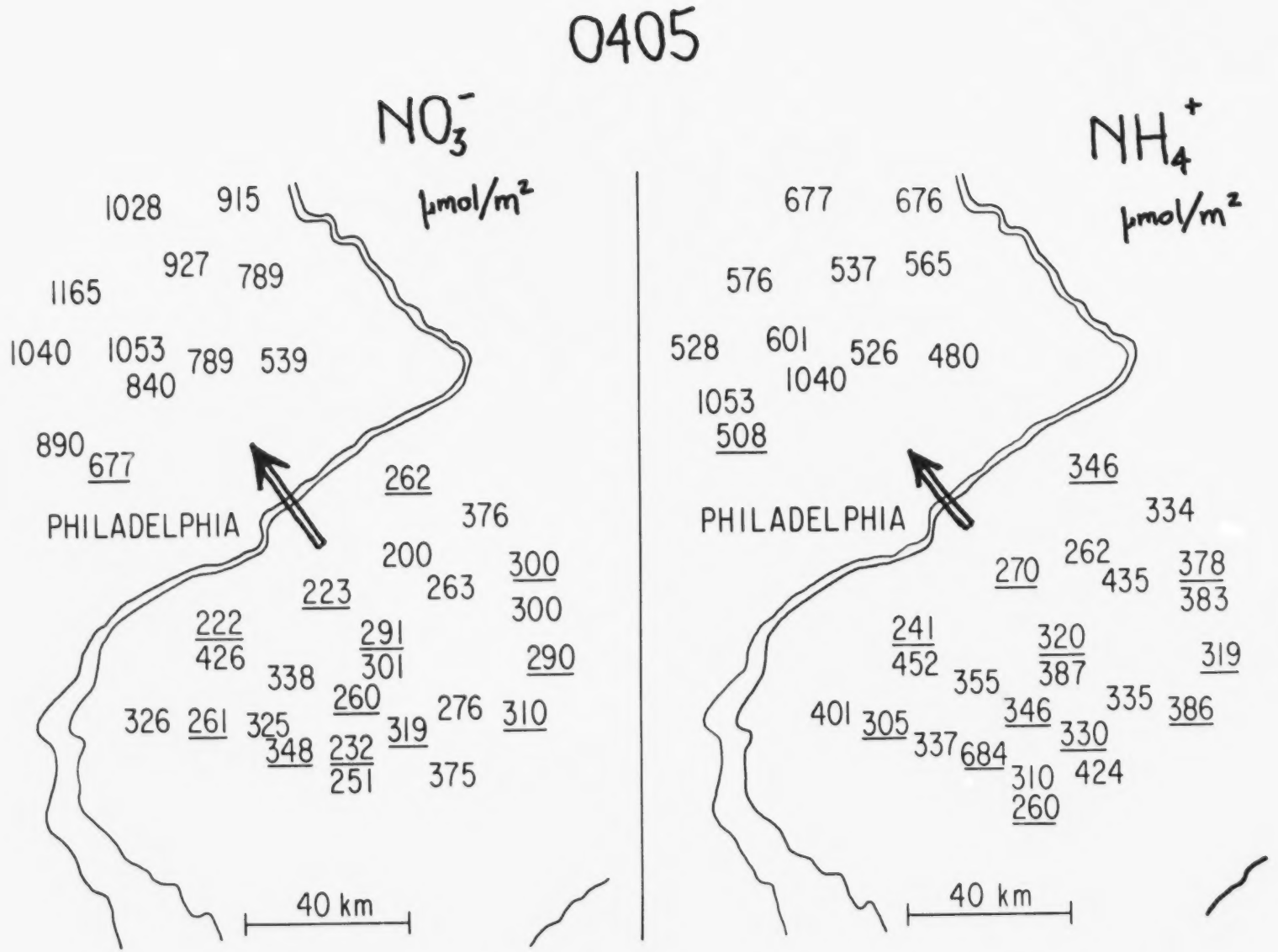

0405
NO_3^-
μmol/m²
1028
915
927
789
1165
1040
1053
789
539
840
890
677
PHILADELPHIA
262
376
200
300
223
263
300
222
426
291
301
290
338
260
326
261
325
276
310
319
348
232
251
375
40 km
NH_4^+
μmol/m²
677
676
576
537
565
528
601
526
480
1040
1053
508
346
PHILADELPHIA
334
270
262
435
378
383
241
452
320
387
319
355
335
386
401
305
346
330
337
684
310
424
260
40 km

Figure 4

estimates of deposition to emission ratios presented earlier. Assuming a peak at 80 km with "mirror" decrease beyond and extrapolating the deposition estimates to 100 km downwind of the Valley, almost 100% of the emitted NO_x may be transformed and deposited as nitric acid on the mesoscale. It should be pointed out that the above mentioned 100% transformation rate may occur only during the precipitation periods and, consequently, for long-term estimates which include both wet and dry periods, the importance of local contributions to the total acid deposition may be deemphasized.

The observed patterns of NH_4^+ deposition is one of the surprises of the field results. It has generally been assumed that the distribution of NH_4^+ is spotty (Hales and Dana, 1979b), perhaps as the consequence of local ammonia sources. In fact, for most of the sampled storms, the coefficient of spatial variation of NH_4^+ is comparable to the ones for the other species. Furthermore, this ion registered an ca. 100% increase in target deposition for 0424 and an ca. 70% increase for 1111 and 0405 (Fig. 4) thus implicating the urban and industrial emissions. The processes responsible for this result are the subject of continuing studies.

With one exception, the deposition of Na^+ mirrors the deposition of Cl^-. This is expected from the proximity of the sampling network to the coast and the predominance of sea salt as the source of Na^+ and Cl^-. The stratified patterns of Na^+ and Cl^- deposition with the monotonic decrease with distance from the coast (Patrinos and Brown, 1984) were another confirmation of the southeasterly transport which dominated the sampled events. Even the slight excess of Cl^- is in agreement with regional

results of the MAP3S/RAINE precipitation chemistry network (The MAP3S/RAINE Research Community, 1982). The exception is storm 0424 which showed considerably higher Cl to Na ratios over the entire network. The cause for this exception is as yet undetermined but is of great interest because of the rising concern regarding the importance of chloride in a wide range of toxic cross media problems (Milot, 1985).

DIAGNOSTIC MODELING OF A PHILADELPHIA STORM

Modeling activities in Task Group C of NAPAP include the development of an Eulerian chemical model to study wet deposition on the mesoscale. The "mesoscale" model is intended to complement the Regional Acid Deposition Model (RADM) currently under development (NCAR, 1984) in its subgrid parameterizations and to identify those processes which are important on the mesoscale. An "engineering" version of the mesoscale model will be made available for assessment purposes. Current plans envision the mesoscale model as the combination of a dynamic model (Kaplan et al., 1982) and a transport-chemical model (Carmichael and Peters, 1984).

As a prelude to the mesoscale modeling activities a series of diagnostic modeling exercises were undertaken (Patrinos and Kleinman, 1984) using a multilayer Lagrangian photochemical model (Kleinman, 1984) with simple scavenging parameterizations. These exercises concentrated on the simulation of conditions prevailing during storm 0405. Their goal was to determine whether chemical pathways thought to be significant both in-cloud and below-cloud coupled with reasonable meteorological and emissions inputs may explain the excess nitrate and sulfate in the

downwind precipitation samples. The model employs a gas phase chemical mechanism adapted from the ERT models (Atkinson et al., 1982; Godden and Lurmann, 1983) and involves 40 chemicals and 65 reactions; an aqueous phase chemistry module is included which involves the dissolution of aerosol sulfate, the liquid phase reactions of SO_2 with O_3 and H_2O_2, the dissolution of gas phase HNO_3 and the production of NO_3^- via the dissolution of N_2O_5.

Storm 0405 was chosen as a test case because it had a substantial "control-target" contrast in wet deposition for both NO_3^- and $SO_4^=$ and presented meteorological features amenable to simple parameterizations in a Lagrangian framework perpendicular to the Delaware river. Steady southeasterly transport prevailed during the storm with low lying stratus clouds (base at 500 m) and with the frontal surface at significantly higher altitude; the surface front remained well to the south during the storm. The Delaware Valley emissions are assumed to enter the clouds through low level convergence and the "control" deposition is due to pollutants from NJ and from the southwest of the sampling area. Table 6 presents some details of "background" pollutants, emissions and model parameters. The calculated excess deposition of NO_3^- and $SO_4^=$ was derived by calculating the amount deposited in a four hour period downwind of the river and integrating over the trajectories spanning the duration of the storm. For NO_3^-, the model calculations explained 60% of the observed excess with the N_2O_5 dissolution dominating the HNO_3 dissolution three to one. For $SO_4^=$, the model explained 75% of the observed excess with the O_3 reaction almost entirely responsible. Modeling of additional storms is planned.

Table 6. Diagnostic Modeling Parameters and Inputs for Storm 0405 Simulation

	H_2O_2	NO_x	O_3	CO	CH_4	RHC
Background Pollutants (ppb)	1	0.1	40	200	1700	19

	SO_2	NO_x	HC
Emissions (ppb in 2.4 km layer)	2.1	4.1	9.3

Model Parameters	
Wind Speed	20 km/h
Storm Duration	24 h
Cloud Temperatures	1-10 °C
Cloud Depth	2 km
Cloud Liquid Water	0.5 gr/kg
Lifetime of Cloudwater	1 h
Vertical Velocity	10 cm/sec

SECTION 5

CONCLUDING REMARKS

This chapter has addressed the issue of the impact of "local" sources on local and mesoscale wet deposition. A sizable portion of the relevant literature (primarily the "open" literature) has been consulted and reviewed and particular emphasis has been placed on recent findings of urban plume effects on mesoscale wetfall chemistry (the Philadelphia study) (Patrinos and Brown 1984; Patrinos et al., 1984). As expected the reviewed scientific results are often contradictory regarding the magnitude and sometimes even the existence of a "local source" problem. Three of the causes for this confusion will be presented and discussed:

1. The complexity of the physical and chemical processes involved in the emission, reaction, scavenging, and deposition of the pollutants implicated in acid wetfall. Examples of meteorological variability seriously affecting the ultimate deposition include the degree of convective activity during precipitation which may, for example, accelerate the oxidation processes and increase the rate of acid production; this may be due to longer residence times of pollutants in-cloud and to the greater availability of oxidants resulting from increased photochemical activity. Another example is the chemical nature of the "background" rain. Since most sulfur emissions occur in the form of SO_2 and its solubility in cloud and rain droplets is a function of pH (and to a lesser extent temperature) the near source wet deposition or liquid phase oxidation will be highly dependent on the chemical history of the precipitating system.

Particularly for area sources, such as urban or industrial centers with rich pollutant mixes, the presence of certain substances may accelerate certain reactions and lead to significant local effects.

2. The paucity of relevant data in the near field of point and area sources. Regional studies on acid wet deposition have relied on precipitation chemistry networks such as MAP3S (The MAP3S/RAINE Research Community, 1982), NADP (Semonin and Bowersox, 1983), CANSAP (Barrie and Sivois, 1982) and others. These networks have purposely located their sites away from large sources (point and area) for more regional representation. Data from these networks have contributed to trend analyses and comprehensive attempts at source-receptor characterizations on a regional scale. Nevertheless, the sink terms based on these networks have been underestimated particularly for nitrate whose characteristic fallout scale from its emission point is shorter than that for sulfur. In recent years, some urban monitoring has been initiated such as in the New York City area (Volchok and Freeswick, 1981), in Philadelphia (Dugan, 1984) and others, but these attempts have not matched the regional networks in resources and funding commitment. Thus, the current state-of-the-knowledge of local source impacts is based on limited wet deposition data, often collected on a "campaign" basis: the deployment of a sampling network during select periods and the extrapolation of the results to seasonal or annual assessments. An alternative approach has been the operation of a few sampling sites in the vicinity of the sources for longer times. Although the results may be more reliable

from a climatological standpoint the limited spatial coverage has often failed to characterize the local source-receptor relationship.

3. Incomplete or inadequate analytical procedures or unsatisfactory QA/QC standards. One of the common weaknesses of earlier studies has been the incomplete chemical analysis of the precipitation samples thus providing only partial and often confusing answers. Insofar as QA/QC procedures are concerned it should be emphasized that the "local source" environment requires more stringent QA/QC standards compared with those for regional networks because of generally poorer air quality (and consequently higher potential dryfall contamination) and severe constraints on the siting of the sampling instruments. Despite the above mentioned shortcomings some general conclusions regarding the local source issue may be reached.

A. The impact of "tall stack" point sources on near field acid wet deposition is small. Tall stacks may be defined as greater than 50 m and the near field as within 30 km. On a budget basis the average percentage of emitted SO_x and NO_x, during the precipitation, which is scavenged in the near field is less than 5%. The percentage for trace metals, however, particularly from smelters may be an order of magnitude higher.

Chloride, whenever present, is also almost totally scavenged in the near field. Below cloud scavenging appears to dominate in this case. Furthermore, even for SO_x the above percentage may under special circumstances be higher. These may include faster oxidation and scavenging rates due to, e.g., favorable convective activity in the vicinity of the source leading to in-cloud scavenging or the presence of certain oxidants or catalysts. As mentioned earlier, since most SO_x is emitted as SO_2 its

near source deposition is very much a function of the background rain chemistry. The opening statement of this conclusion needs to be qualified further. Even though from a budget point of view the impact may be small the contrast between "target" near field and "control" background particularly in relatively pristine areas may be striking. Beyound the 30 km distance defined as near field for point sources it may be argued that the source-receptor problem assumes regional characteristics.

B. The impact of area sources, such as large urban and industrial complexes on mesoscale wet deposition is significant. Area sources may be defined as population sources of ca. one million with SO_x, NO_x, and HC emissions in the 10^5 tons/year for each from a variety of industrial, residential, and transportation sources. Two deposition scales have been identified with regard to those sources. The first is the area source itself. Wet deposition on that scale is dominated by below cloud scavenging. Due to higher pollutant air concentrations sulfates and nitrates in rainwater would be higher than regional values. However, due to high concentrations of neutralizing agents, such as Ca^{2+}, net acidity may not be substantially higher than regional values and may in fact be lower at times.

The second deposition scale is the mesoscale defined as ca. 100km. The impact of the area source emissions was found to be maximum on that scale. It appears that, particularly for NO_x, a significant percentage (>50%) is transformed to nitric acid and deposited on the mesoscale. The percentage for SO_x is smaller, but still significant. The nitrate deposition primarily implicates the significant transportation sources which are at low elevations and diffuse. Therefore, they may mix

thoroughly with other pollutants and oxidants and as they travel downwind may become incorporated into clouds leading to faster transformation and scavenging rates. Some evidence of the impact of the urban plume on downwind wet NH_4^+ deposition is also present.

C. Preliminary indications, based on limited but reliable field data, have shown that the impact of primary sulfates on local and mesoscale wet deposition is minimal.

REFERENCES

American Meteorological Society. 1981. METROMEX: A review and summary, Meteorological monograph (edited by S.A. Changnon, Jr.), 18, 40, AMS, Boston, MA, 181 pp.

Andersson, T. 1969. Small-scale variations of the contamination of rain caused by washout from the low layers of the atmosphere, Tellus, XXI, 5, 685-692.

Atkinson, R., A.C. Lloyd, and L. Winges. 1982. A new chemical mechanism for hydrocarbon/NO_x/SO_x photo-oxidation suitable for inclusion in atmospheric simulation models, Atmos. Environ. 16, 1341-1355.

Baer, N.S., G. Kirmeyer, and J.E. Yocom. 1984. Critical Assessment Review Papers, Chapter E-7, Vol. 2, 7.1-7.38, EPA-600/8-83-016BF.

Barrie, L.A. 1980. The fate of particulate emissions from an isolated power plant in the oil sands areas of western Canada, in Annals of the New York Academy of Sciences, (Eds. T.J. Kneip and P.J. Lioy), 338, 434-452.

Barrie, L.A., and A. Sirois. 1982. An analysis and assessment of precipitation chemistry measurements made by CANSAP: 1977-1980, Report AQRB-82-003-T of the Atmospheric Environment Service, 4905 Dufferin Street, Downsview, Ontario, Canada

Benkovitz, C.M. 1980. MAP3S/RAINE emissions inventory progress report. BNL 51378, Brookhaven National Laboratory, Upton, NY 11973.

Benkovitz, C.M. 1982. Compilation of an inventory of anthropogenic emissions in the United States and Canada. Atmos. Environ. 16:1551-1556.

Benarie, M. 1976. Transport of pollutants considered from the point of view of a short and medium-range material balance, Water, Air and Soil Pollut., 6, 329-338.

Bielke, S., and H.W. Georgii. 1968. Investigation on the incorporation of sulphur dioxide into fog- and rain droplets, Tellus, 20, 435-442.

Bridgman, H.A. 1984. Mesoscale spatial variability of sulfate in air and rainwater at St. Louis, Water, Air and Soil Pollut., 22, 153-172.

Cadle, S.H. 1984. The composition of dew in an urban area, in The Meteorology of Acid Deposition (editor, P.J. Samson), Air Pollution Control Association, Pittsburgh, PA 15230, pp. 17-29.

Calvert, J.G., and W.R. Stockwell. 1983. Acid generation in the troposphere by gas-phase chemistry, Environ. Sci. Technol., 17, 9, 428A-443A.

Carmichael, G.R. and L.K. Peters. 1984. An Eulerian transport/transformation/ removal model for SO_2 and sulfate - I. Model development, Atmos. Environ., 18, 5, 937-951.

Chan, W.H., C.U. Ro, M.A. Lusis, and R.J. Vet. 1982. Impact of the INCO nickel smelter emissions on precipitation quality in the Sudbury area, Atmos. Environ., 16, 4, 801-814.

Chan, W.H., R.J. Vet, C.U. Ro, A.J.S. Tang, and M.A. Lusis. 1984a. Impact of INCO smelter emissions on wet and dry deposition in the Sudbury area, Atmos. Environ., 18, 5, 1001-1008.

Chan, W.H., R.J. Vet, C.U. Ro, A.J.S. Tang, and M.A. Lusis. 1984b. Long-term precipitation quality and wet deposition fields in the Sudbury basin, Atmos. Environ., 18, 6, 1175-1188.

Cleveland, W.S., R.J. McRae. 1978. Weekday-weekend ozone concentrations in the Northeast United States, Environ. Sci. Technol., 12, 5, 559-563.

Cleveland, W.S., and T.E. Graedel. 1979. Photochemical air pollution in the Northeast United States, Science, 204, 1273-1278, 1979.

Dana, M.T., J.M. Hales, and M.A. Wolf. 1975. Rain scavenging of SO_2 and sulfate from power plant plumes, J. Geophys. Res., 80, 4119-4129.

Dana, M.T., D.R. Drewes, D.W. Glover, and J.M. Hales. 1976. Precipitation scavenging of fossil-fuel effluents, Report EPA-600/4-76-031, Battelle Pac. Northwest Lab., Richland, Washington.

Dana, M.T. 1980. SO_2 versus sulfate wet deposition in the Eastern United States, J. Geophys. Res., 85, C8, 4475-4480.

Dana, M.T., and A.A.N. Patrinos. 1983. Scavenging measurements near large point sources: a review and evaluation, in Precipitation Scavenging, Dry Deposition, and Resuspension, Vol. 1, Precipitation Scavenging (Editors, H.R. Pruppacher, R.G. Semonin, and W.G.N. Slinn), Elsevier, New York, pp. 335-347.

Dana, M.T., A.A.N. Patrinos, E.G. Chapman, and J.M. Thorp. 1984. Wintertime precipitation chemistry in North Georgia, in Meterological Aspects of Acid Rain, Vol. 1, Acid Precipitation Series (editor C.M. Bhumralkar), Butterworth Publishers, MA. pp 119-144.

Dana, M.T. 1985. The contribution of sulfur-IV to sulfur wet deposition in the eastern United States. Submitted to J. Geophys. Res.

Dasch, J.M., and S.H. Cadle. 1984. The effect of local emissions on wet and dry deposition in southeastern Michigan, Atmos. Environ., 18, 5, 1009-1015.

Dasch, J.M., S.H. Cadle, and G.T. Wolff. 1984. Summertime study of acid deposition in the Detroit area, Water, Air, and Soil Pollut., 21, 51-69.

Davies, T.D. 1976. Precipitation scavenging of sulphur dioxide in an industrial area, Atmos. Environ., 10, 879-890.

Davies, T.D. 1979. Dissolved sulpher dioxide and sulphate in urban and rural precipitation (Norfolk, U.K.) Atmos. Environ., 13, 1275-1285.

DeWys, J.N., A.C. Hill, and E. Robinson. 1978. Assessment of the fate of sulfur dioxide from a point source, Atmos. Environ., 12, 633-639.

Draxler, R.R. 1983. Lagrangian meteorology and measurements of acidic precipitation at Washington, D.C., Atmos. Environ., 17, 12, 2525-2531.

Dugan, Neil. 1984. Personal Communication, Air Management Services Laboratory, Philadelphia, PA.

Enger, L., and U. Högström. 1979. Dispersion and wet deposition of sulfur from a power plant plume, Atmos. Environ., 13, 797-810.

EPA. 1982. Emission inventories for urban airshed model application in the Philadelphia AQCR, EPA-450/4-82-005, Research Triangle Park, NC.

Forrest, J., R. Garber, and L. Newman. 1979. Formation of sulfate, ammonium and nitrate in an oil-fired power plant plume, Atmos. Environ., 13, 1287-1297.

Forrest, J., R.W. Garber, and L. Newman. 1981. Conversion rates in power plant plumes based on filter pack data: The coal-fired Cumberland plume, Atmos. Environ., 15, 10/11, 2273-2282.

Gatz, D.F. 1980. Associations and mesoscale spatial relationships among rainwater constituents, J. Geophys. Res., 85, C10, 5588-5598.

Gillani, N.V., R.B. Husar, J.D. Husar, and D.E. Patterson. 1978. Project MISTT: Kinetics of particulate sulfur formation in a power plant plume out to 300 km, Atmos. Environ., 12, 589-598.

Gillani, N.V., S. Kohli, and W.E. Wilson. 1981. Gas-to-particle conversion of sulfur in power plant plumes - I. parameterization of the conversion rate for dry, moderately polluted ambient conditions, Atmos. Environ., 15, 10/11, 22932313.

Godden, D. and L. Lurmann. 1983. Development of the PLMSTAR model and its application to ozone episode conditions in the South Coast Air Basin. ERT Document No. P-A702-200, ERT, Westlake Village, CA.

Gorham, E., F.B. Martin, and J.T. Litzau. 1984. Acid rain: ionic correlations in the eastern United States, Science, 225, 407-409.

Granat, L., and H. Rodhe. 1973. A study of fallout by precipitation around an oil-fired power plant, Atmos. Environ., 7, 781-792.

Gregory, G.L. 1976. NASAS Report TN D-8352, NTIS, Springfield, VA 22151.
Hales, J.M. 1978. Wet removal of sulfur compounds from the atmosphere, Atmos. Environ., 12, 389-399.

Hales, J.M., and S.L. Sutter. 1973. Solubility of sulfur dioxide in water at low concentrations, Atmos. Environ., 7, 997-1001.

Hales, J.M., J.M. Thorp, and M.A. Wolf. 1971. Field investigation of sulfur dioxide washout from the plume of a large coal-fired power plant by natural precipitation, Final report, EPA Contract 22-69-150, Battelle Pacific Northwest Labs, Richland, Washington.

Hales, J.M., and M.T. Dana. 1979a. Regional scale deposition of sulfur dioxide by precipitation scavenging, Atmos. Environ., 13, 1121-1132.

Hales, J.M., and M.T. Dana. 1979b. Precipitation scavenging of urban pollutants by convective storm systems, J. Appl. Meteorol., 18, 3, 294-316.

Hegg, D.A., and P.V. Hobbs. 1978. Oxidation of sulfur dioxide in aqueous systems with particular reference to the atmosphere, Atmos. Environ., 12, 241-253.

Hegg, D.A., P.V. Hobbs, and L.F. Radke. 1984. Measurements of the scav enging of sulfate and nitrate in clouds, Atmos. Environ., 18, 9, 1939-1946.

Högström, U. 1974. Wet fallout of sulfurous pollutants emitted from a city during rain or snow, Atmos. Environ., 8, 1291-1303.

Holt, B.D. E. Nielsen, and R. Kumar. 1983. Oxygen-18 estimation of primary sulfate in total sulfate scavenged by rain from a power plant plume, in Precipitation Scavenging, Dry Deposition and Resuspension, Vol 1, Precipitation Scavenging (editors, H.R. Pruppacher, R.G. Semonin, and W.G.N. Slinn), Elsevier, New York, pp. 357-368.

Hlavay, J. and G.G. Guibault. 1978. Detection of HCl gas in ambient air with a coated piezoelectric quartz crystal. Anal. Chem. 50:965-967.

Hutcheson, M.R., F.P. Hall, Jr. 1974. Sulfate washout from a coal fired power plant plume, Atmos. Environ., 8, 23-28.

Iapalucci, T.L., R.J. Demski and D. Bienstock. 1969. Chlorine in coal combustion. Bur. Mines Rep. Invest., 7260, Pittsburgh, PA.

Johnson, A.H., and T.G. Siccama. 1983. Acid deposition and forest decline, Environ. Sci. Technol., 17, 7, 294A-305A.

Kaplan, M.L., J.W. Zack, V.C. Wong, and J.J. Tuccillo. 1982. Initial results from a mesoscale atmospheric simulation system and comparison with the AVE-SESAME I data set, Monthly Weather Review, 100, 1564-1590.

Kleinman, L.I. 1984. A regional scale Lagrangian nonlinear chemistry model for acid deposition. Proceedings of Fourth Joint Conference of Air Pollution Meteorology, October 16-19, 1984, American Meteorological Society, Boston, MA.

Larson, T.V., R.J. Charlson, E.J. Knudson, G.D. Christian, and H. Harrison. 1975. The influence of a sulfur dioxide point source on the rain chemistry of a single storm in the Puget Sound region, Water, Air, and Soil Pollut., 4, 319-328.

Levine, S.Z., and S.E. Schwartz. 1982. In-cloud and below-cloud scavenging of nitric acid vapor, Atmos. Environ., 16, 7, 1725-1734.

Li. T.Y., and H.E. Landsberg. 1975. Rainwater pH close to a major power plant, Atmos. Environ., 9, 81-88.

Likens, G.E., R.E. Wright, J.N. Galloway, and T.J. Butler. 1979. Acid Rain, Scientific American, 241, 4, 43-51.

Liljestrand, H.M., and J.J. Morgan. 1981. Spatial variations of acid precipitation in Southern California, Environ. Sci. Technol., 15, 3, 333-339.

Lipfert, F.W., L.R. Dupuis, and L. Alvarez. 1984. Urban and local source effects on precipitation chemistry. BNL 34565, Brookhaven National Laboratory, Upton, NY, 20 pp.

Lusis, M.A., K.G. Anlauf, L.A. Barrie, and H.A. Wiebe. 1978. Plume chemistry studies at a northern Alberta power plant, Atmos. Environ., 12, 2429-2437.

Lusis, M.A., W.H. Chan, A.J.S. Tang, and N.D. Johnson. 1983. Scavenging rates of sulfur and trace metals from a smelter plume, in Precipitation Scavenging, Dry Deposition, and Resuspension, Vol. 1 Precipitaton Scavenging (editors, H.R. Pruppacher, R.G. Semonin, and W.G.N. Slinn), Elsevier, New York, pp. 369-382.

Millan, M.M., S.C. Barton, N.D. Johnson, B. Weisman, M. Lusis, W. Chan, and R. Vet. 1982. Rain scavenging from tall stack plumes: a new experimental approach, Atmos. Environ., 16, 2709-2714.

Milot, C. 1985. Multimedia maneuvers: Shifting tactics for controlling shifting pollutants. Science News 127:124-126.

Munn, R.E., G.E. Likens, B. Weisman, J. Hornbeck, C.W. Martin, F.H. Borman, G.W. Oehlert, R. Bloxam. 1982. A climatological analysis of the Hubbard Brook (New Hampshire) precipitation chemistry data, Grant DE-FG01-SOEV-10455, prepared for U.S. DOE, Washington, DC.

NCAR. 1984. Regional acid deposition: Models and physical processes, the NCAR Acid Deposition Modeling Project, EPA Report EPA-600/3-84-0541, Research Triangle Park, NC.

Parungo, F.P., and R.F. Pueschel. 1980. Conversion of nitrogen oxide gases to nitrate particles in oil refinery plumes, J. Geophys. Res., 85, C8, 4507-4511.

Parungo, F.P., R.F. Pueschel, and D.L. Wellman. 1980. Chemical characteristics of oil refinery plumes in Los Angeles, Atmos. Environ., 14, 509-522.

Patrinos, A.A.N., M.T. Dana, and R.E. Saylor. 1983. Wetfall chemistry studies around a large coal-fired power plant in the southeastern United States, J. Geophys. Res., 88, C13, 8585-8612.

Patrinos, A.A.N. 1983. Mesoscale acid deposition study. BNL 34494, Brookhaven National Laboratory, Upton NY 11973, 70 pp.

Patrinos, A.A.N., 1985. The influence of urban and industrial emissions on mesoscale precipitation quality, J. of Air Pollut. Control Assoc., 35, 719-727.

Patrinos, A.A.N., and R.M. Brown. 1984. Mesoscale wetfall chemistry around Philadelphia during frontal storms, Geophys. Res. Lett., 11, 5, 561-564.

Patrinos, A.A.N. 1984. Interim quality assurance and quality control activities during the Philadelphia field study. BNL 35715, Brookhaven National Laboratory, Upton, NY 11973. 16 pp.

Patrinos, A.A.N, and L.I. Kleinman. 1984. Diagnostic modeling of pollutant transformation and wet deposition on the urban scale, Transactions, American Geophysical Union, Vol. 65, 45, p. 844.

Penkett, S.A., B.M.R. Jones, K.A. Brice, and A.E.J. Eggleton. 1979. The importance of atmospheric ozone and hydrogen peroxide in oxidising sulphur dioxide in cloud and rainwater, Atmos. Environ., 13, 123-137.

Platt, U.V., A.M. Winer, H.W. Biermann, R. Atkinson, and J.N. Pitts, Jr. 1984. Measurement of nitrate radical concentrations in continental air. E.S. & T. 18:365-369.

Pratt, G.C., M. Coscio, D.W. Gardner, B.I. Chevone, and S.V. Krupa. 1983. An analysis of the chemical properties of rain in Minnesota, Atmos. Environ., 17, 2, 347-355.

Raynor, G.S. and J.V. Hayes. 1982. Variation in chemical wet deposition with meteorological conditions, Atmos. Environ., 16, 1647-1656.
Richards, L. W. 1983. Comments on the oxidation of NO_2 to nitrate-day and night, Atmos. Environ., 17, 2, 397-402.

Rodhe, H. 1970. On the residence time of anthoropogenic sulfur in the atmosphere, Tellus, XXII, 1, 137-139.

Rodhe, H., C. Persson, and O. Akesson. 1972. An investigation into regional transport of soot and sulfate aerosols, Atmos. Environ., 6, 675-693.

Scheider, W.A., D.S. Jeffries, and P.J. Dillon. 1981. Bulk deposition in the Sudbury and Muskoka-Haliburton areas of Ontario during the shutdown of INCO Ltd in Sudbury, Atmos. Environ., 15, 6, 945-956.

Schiermeir, F.A. 1978. Air monitoring milestones: RAPS' field measurements are in, Environ. Sci. and Technology, 12, 644-651.

Schwartz, S.E. 1984. Gas-aqueous reactions of sulfur and nitrogen oxides in liquid-water clouds. In SO_2, NO, and NO_2 oxidation mechanisms: atmospheric conditions, J.B. Calvert, ed., Butterworth, Boston, MA, pp. 173-208.

Scott, B.C. 1978. Parameterization of sulfate removal by precipitation, J. Appl. Meteor., 17, 1375-1389.

Scott, B.C. and N.S. Laulainen. 1978. On the concentration of sulfate in precipitation. J. Appl. Meteor., 18:138-147.

Semonin, R.G., and V.C. Bowersox. 1983. Characterization of the inorganic chemistry of the precipitation of North America, in Precipitation Scavenging, Dry Deposition and Resuspension, Vol. 1, Precipitation Scavenging (editors, H.R. Pruppacher, R.G. Semonin, and W.G.N. Slinn), Elsevier, New York, pp. 191201.

Sexton, K. and H.H. Westberg. 1983. Ambient hydrocarbon and ozone concentrations near a refinery. EPA-600/S3-83-025, Research Triangle Park, NC.

Shaw, R.W. 1982. Deposition of atmospheric acid from local and distant sources at a rural site in Nova Scotia, Atmos. Environ., 16, 2, 337-348.

Slanina, J., F.G. Romer, and W.A.H. Asman. 1983. Estimation of wet deposition from a plume of a powerplant and the corresponding background concentration, in Precipitation Scavenging, Dry Deposition, and Resuspension, Vol. 1, Precipitation Scavenging (editors, H.R. Pruppacher, R.G. Semonin, and W.G.N. Slinn), Elsevier, New York, 349-356.

Spaite, P.W. and M.F. Szabo. 1982. Acid rain: commentary on controversial issues and observations on the role of fuel burning. NTIS Publication No. DE82 016914. U.S. Dept. of Energy, Morgantown, WV.

Spicer, C.W. 1977. The fate of nitrogen oxides in the atmosphere, Advances in Environmental Science and Technology (edited by Pitts & Metcalf), Wiley, New York, 7, 163-261.

Spicer, C.W. 1982. Nitrogen oxide reactions in the urban plume of Boston, Science, 215, 1095-1097.

Stamm, A.J., P. Caplan and R.A. Hinrichs. 1984. Rain chemistry under the plume from an oil-fired power plant - a case study, Atmos. Environ., 18, 4, 817-823.

Stevenson, C.M. 1968. An analysis of the chemical composition of rainwater and air over the British Isles and Eire for the years 1959-1964, Quart. J. Roy. Met. Soc., 94, 56-70.

Summers, P.W. and B. Hitchon. 1973. Source and budget of sulfate in precipitation from central Alberta, Canada, J. of Air Pollut. Control Assoc., 23, 3, 194-199.

Summers, P.W., and D.M. Whelpdale. 1976. Acid precipitation in Canada, Water, Air and Soil Pollut., 12, 171-185.

The MAP3S/RAINE Research Community. 1982. The MAP3S/RAINE precipitation chemistry network: statistical overview for the period 1976-1980. Atmos. Environ. 16:1603-1631.

Volchok, H.L., and D.C. Freeswick. 1981. Environmental Measurements Laboratory Regional Baseline Station, Chester, New Jersey, EML-399, Environmental Measurements Laboratory, U.S. Dept. of Energy, New York, NY.

Watt, W.D., D. Scott, and S. Ray. 1979. Acidification and other chemical changes in Halifax County Lakes after 21 years, Limnol. Oceanogr., 24, 1154-1161.

West, P.W., and G.C. Gaeke. 1956. Fixation of sulphur dioxide as disulphiomercurate (II) and subsequent colorimetric estimation, Analyt. Chem., 28, 1816-1819.

Wiebe, H.A., and D.M. Whelpdale. 1977. Precipitation scavenging from a tallstack plume, Precipitation Scavenging, Rep. CONF-741003, pp. 118-126, U.S. Dep. Energ., Washington, DC.

Wiltshire, J.F. 1979. The long range transport of atmospheric acids; a sulphur budget for Nova Scotia. Rep. EPS-5-AR-77-8. Environmental Protection Service, Halifax, Nova Scotia, Canada B3J 1M5, 114 pp.